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A NEW VECTOR METHOD IN INTEGRAL EQUATIONS

By Frank L. Hitchcock and Norbert Wiener

1. **Introduction.** It is a well recognized fact that the theory of the Fredholm integral equation is essentially a generalization of the theory of the linear vector function and of the linear vector equation. The Fredholm equation

$$r(x)-\lambda\int_a^b K(x,y)r(y)dy=s(x) \tag{1}$$

is the precise analogue of the linear vector equation

$$T.r=(I-\lambda K).r=s \tag{2}$$

where K is a dyadic, I is the idemfactor, s a given vector, and r a required vector; hence T is also a dyadic and the homogeneous equations

$$r(x)-\lambda\int_a^b K(x,y)r(y)dy=0 \tag{3}$$

and

$$T.r=0 \tag{4}$$

correspond. The Schmidt-Hilbert theory of (1) and (3) is based on the reduction of the dyadic T to the normal form

$$c_1i_1i_1'+c_2i_2i_2'+\ldots+c_ni_ni_n' \tag{5}$$

where the i's are unit vectors such that each vector without the stroke is perpendicular to the remaining stroked vectors.

Thus the customary treatment of (1) and (3) depends upon the determination of certain vectors related to a dyadic, and connected by certain relations of orthogonality. If K is a self-conjugate dyadic, the vectors with the stroke will coincide with those without the stroke, and will in fact be unit vectors directed along the axes of the quadric

$$r.T.r=1 \tag{6}$$

Now the axes of a quadric are merely special conjugate diameters

which happen to be orthogonal. Two vectors a and a' will be directed along conjugate diameters if

$$a.T.a'=0 \tag{7}$$

Development in terms of conjugate diameters hence becomes a natural generalization of development in terms of axes.

There is a theorem due to Gibbs[1] to the effect that if $a_1, a_2, \ldots a_n$ are vectors such that any pair satisfy (7) while for each of them such an equation holds as

$$a.T.a=1 \tag{8}$$

we may write

$$T^{-1}=a_1a_1+a_2a_2+\ldots+a_na_n. \tag{9}$$

Hence we may obtain as the solution of (2), if T is a self-conjugate dyadic,

$$r=a_1a_1.s+a_2a_2.s+\ldots+a_na_n.s \tag{10}$$

If T is not self-conjugate we may still get a similar expansion for the solution of (2). Let there be two sets of vectors

$$a_1, a_2, \ldots a_n \tag{11}$$

$$a_1', a_2', \ldots a_n' \tag{12}$$

such that

$$a_i.T.a_j'=0 \quad \text{whenever } i\neq j. \tag{13}$$

If we assume

$$r=a_1'x_1+a_2'x_2+\ldots+a_n'x_n \tag{14}$$

equation (2) becomes

$$x_1T.a_1'+x_2T.a_2'+\ldots+x_nT.a_n'=s \tag{15}$$

and if we multiply by a_j we have

$$x_ja_j.T.a_j'=a_j.s \tag{16}$$

whence we have a formal solution of (2)

$$r=\frac{a_1'a_1.s}{a_1.T.a_1'}+\frac{a_2'a_2.s}{a_2.T.a_2'}+\ldots+\frac{a_n'a_n.s}{a_n.T.a_n'} \tag{17}$$

This becomes a formal solution of (1) if we define

[1] Gibbs-Wilson, Vector Analysis, p. 378.

$$a.T.a' = \int_a^b a(x)\,[a'(x) - \lambda \int_a^b K(x,y)a'(y)dy\,]dx \tag{18}$$

$$a.s = \int_a^b a(x)s(x)dx, \quad [a = a(x), \text{ etc.}] \tag{19}$$

and allow the integer n to become infinite.

2. **Construction of a biconjoint set of functions.**[2] A biconjoint set of functions is a set defined by (11), (12), (13) and (18). We may construct the functions a and a' in the following manner: let $i_1, i_2, \ldots i_n, \ldots$ *ad inf.* be *any* linearly independent set of functions, not in general orthogonal, and compute the numbers, $i_p.T.i_q$, which, for brevity, we may call a_{pq}; and form the determinant

$$\begin{vmatrix} a_{11}, & a_{12}, & a_{13}, & \ldots & a_{1n} \\ a_{21}, & a_{22}, & a_{23}, & \ldots & a_{2n} \\ a_{31}, & a_{32}, & a_{33}, & \ldots & a_{3n} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ a_{n1}, & a_{n2}, & a_{n3}, & \ldots & a_{nn} \end{vmatrix} \tag{20}$$

Now let $A_{1n}, A_{2n}, \ldots A_{nn}$ be the co-factors of the elements $a_{1n}, a_{2n}, \ldots a_{nn}$ in the above determinant, and let $A_{n1}, A_{n2}, \ldots A_{nn}$ be the co-factors of $a_{n1}, a_{n2}, \ldots a_{nn}$. Write

$$a_n = i_1 A_{1n} + i_2 A_{2n} + \ldots + i_n A_{nn}. \tag{21}$$

$$a_n' = i_2 A_{n1} + i_2 A_{n2} + \ldots + i_n A_{nn} \tag{22}$$

In general we define A_{pq} to be the co-factor of the element a_{pq} in the determinant of order k formed as above, by writing k for n, where k is equal to the larger of the two integers p and q when p and q are unequal, and equal to p and q when they are equal. We say that the functions $a_1, a_2, \ldots a_n, \ldots$ *ad inf.* and $a_1', a_2', \ldots a_n', \ldots$ *ad inf.* thus formed constitute a biconjoint set.

[2] In the symmetrical case this becomes nearly identical with a theory due to Mrs. Anna Pell. *Cf.* "Biorthogonal Systems of Functions" and "Applications of Biorthogonal Systems of Functions to Integral Equations," Trans. Am. Math. Soc., 1911.

Proof. We have to show that $a_p.T.a_q' = 0$ when $p \neq q$. Suppose $p<q$ and expand a_p. We have by definition

$$\begin{aligned} a_p.T.a_q' &= A_{1p}i_1.T.a_q' + A_{2p}i_2.T.a_q' + \ldots + A_{pp}i_p.T.a_q' \\ &= A_{1p}[a_{11}A_{q1} + a_{12}A_{q2} + \ldots + a_{1q}A_{qq}] \\ &+ A_{2p}[a_{21}A_{q1} + a_{22}A_{q2} + \ldots + a_{2q}A_{qq}] \\ &+ \ldots + \ldots \\ &+ A_{pp}[a_{p1}A_{q1} + a_{p2}A_{q2} + \ldots + a_{pq}A_{qq}] \end{aligned}$$

But each expression in brackets consists of the sum of the cofactors of the elements $a_{q1}, a_{q2}, \ldots a_{qq}$ from the determinant $A_{(q+1)(q+1)}$ each multiplied by the elements of another row from the same determinant. These sums therefore vanish, and the theorem is proved if $p<q$.

If $p>q$, we expand a_q' first instead of last, and prove in like manner.

Corollary. By proceeding in a similar manner when $p=q$ we find

$$a_n.T.a_n' = A_{nn}A_{(n+1)(n+1)} \tag{23}$$

3. **Explicit formal solution of the integral equation (1).** Suppose now the quantities $i_p.s$, that is $\int_a^b i_p(x)s(x)dx$, to have been computed, and call them for brevity b_p. The formal solution (17), by virtue of (21), (22) and (23) becomes

$$\begin{aligned} \tau(x) = &\frac{1}{A_{11}A_{22}}\ i_1A_{11}b_1 \\ &+\frac{1}{A_{22}A_{33}}\ [i_1A_{21}+i_2A_{22}]\ [A_{12}b_1+A_{22}b_2] \\ &+\frac{1}{A_{33}A_{44}}\ [i_1A_{31}+i_2A_{32}+i_3A_{33}]\ [A_{13}b_1+A_{23}b_2+A_{33}b_3] \\ &+\ldots\ +\ldots \\ &+\frac{1}{A_{nn}A_{(n+1)(n+1)}}\ [i_1A_{n1}+i_2A_{n2}+\ldots+i_nA_{nn}] \\ &\qquad [A_{1n}b_1+A_{2n}b_2+\ldots+A_{nn}b_n] \\ &+\ldots \textit{ad inf.} \end{aligned} \tag{24}$$

We note that $A_{11}=1$, $A_{22}=a_{11}$, $A_{21}=-a_{12}$, $A_{12}=-a_{21}$, while A_{nn} is a determinant of order $n-1$. The quantities b, by definition, involve the evaluation of a single definite integral. The quantities a_{pq} involve the evaluation of a double integral and a single integral, as in (18), namely

$$a_{pq}=i_p.T.i_q=\int_a^b i_p(x)i_q(x)dx-\lambda\int_a^b\int_a^b K(x,y)i_p(x)i_q(y)dy\,dx. \tag{25}$$

where the functions $i(x)$ are any linearly independent closed set.

4. **Discussion of the solution when n is finite.** If K is a self-conjugate dyadic, a_1 and a_1', a_2 and a_2', etc., will coincide. If T is a dyadic of positive definite form, it may further be proved that none of the denominators in (17) can vanish. Now we may transform (2) into the equatioh

$$T_c.Tr=T_c.s \tag{26}$$

by operating on both sides with T_c, the dyadic conjugate to T. If T is a complete dyadic $T_c.T$ will be an essentially positive dyadic. We have hence a perfectly general method of solving the linear vector equation when n is finite.

The homogeneous equation (4) will have only 0 as its solution unless the determinant of T vanishes, when it will have other solutions. The solutions of (4) will be completely characterized by the fact that they will be orthogonal to every vector of the form $f.T$. We may hence determine the solutions of (4) by

(1) taking any set of linearly independent vectors $i_1, \ldots i_n$;

(2) forming $i_1.T, \ldots i_n.T$;

(3) finding a vector perpendicular to every $i.T$.[3]

One way of finding a vector perpendicular to every $i.T$ is to select from the vectors $i.T$ a linearly independent set, which we may call $f_1, f_2, \ldots f_k, \ldots$; then compute the numbers $f_p.f_q$ which we may call f_{pq}; and let F_{pq} be the cofactor of f_{pq} defined like A_{pq} above. The vectors

$$g_k=f_1F_{1k}+f_2F_{2k}+\ldots+f_kF_{kk} \tag{27}$$

[3]This method of solving (4) is in principle that of Hamilton (Elements of Quaternions, Vol. I, 2d ed., p. 498).

will be perpendicular to each other. (Proof as above.) We then select some vector (or vectors) h not linearly dependent on the vectors g, and form

$$l=h-\Sigma\frac{gg.h}{g.g} \tag{28}$$

This latter vector will satisfy (4).

The methods so far discussed are in no wise restricted to $N-$space. It might be expected that they would carry over almost unchanged to function space. It is the purpose of this paper to show that this surmise is correct. A new method of solving integral equations is thereby developed.

5. **Second formal solution of the integral equation (1).** With the same notation and meaning for $b_1, b_2, \ldots, b_n, \ldots$ as above, form the functions

$$\begin{aligned} b_1&=i_1b_2-i_2b_1\\ b_2&=i_2b_3-i_3b_2\\ &\cdots\cdots\cdots\\ b_n&=i_nb_{(n+1)}-i_{(n+1)}b_n\\ &\cdots\cdots\cdots\cdots \end{aligned} \tag{29}$$

We then have for any value of n

$$b_n.s=b_{(n+1)}i_n.s-b_ni_{(n+1)}.s=0 \tag{30}$$

by definition of the b's. That is, s is orthogonal to every b. Again, form the functions $T_c.b=b.T$, which we may call $f_1, f_2, \ldots f_n, \ldots$. Finally, form a function orthogonal to every f. This latter function will be of the form μr where μ is a constant and r is a solution of (1). Thus the explicit formal solution is

$$\mu r=h-\Sigma\frac{gg.h}{g.g} \tag{31}$$

where h is any function not linearly dependent on the f's, and the g's are given by (27). The constant μ may be found by substitution in the original equation.[4]

[4]Regarded as a solution of the linear vector equation, this method is in principle that of Hamilton. (Elements of Quaternions, Vol. I, 2d ed., p. 485).

The function s is not in general linearly dependent on the f's. If not, we may write $h=s$ so that $h.g=s.g$.

6. **Convergence in the mean.** Using a slight modification of a notation due to Hurwitz, we shall write[8]

$$f(x) \sim g(x) \tag{32}$$

if

$$\int_a^b \Big(f(x)-g(x)\Big)^2\,dx=0$$

We shall say that $f_n(x)$ converges in the mean to $f(x)$ if

$$\lim_{n\to\infty}\int_a^b \Big(f_n(x)-f(x)\Big)^2\,dx=0$$

and that

$$\sum_1^\infty a_i\phi_i(x) \sim f(x) \tag{33}$$

if

$$\lim_{n\to\infty}\int_a^b \Big(f(x)-\sum_1^n a_i\phi_i(x)\Big)^2 dx=0$$

Let $f(x)$ and $g(x)$ be any two functions such that $\int_a^b \Big(f(x)\Big)^2\,dx$ and $\int_a^b \Big(g(x)\Big)^2\,dx$ exist. Then

$$2\Big|f(x)g(x)\Big| \leq \Big(f(x)\Big)^2 + \Big(g(x)\Big)^2 \tag{34}$$

and hence $\overline{\int_a^b}\Big|f(x)g(x)\Big|\,dx$ exists. Then the quadratic form

$$\int_a^b \Big(f(x)\Big)^2 dx+2\lambda\overline{\int_a^b}\Big|f(x)g(x)\Big|\,dx+\lambda^2\int_a^b \Big(g(x)\Big)^2\,dx \tag{35}$$

[8] *Cf.* M. Plancherel, Rend. Cir. Math. Palermo, 30, pp. 289-335. In all that follows integration will be taken in the sense of Lebesgue.

will clearly exist and be positive definite, so that its discriminant

$$\left(\overline{\int}_a^b \left| f(x)g(x) \right| dx\right)^2 - \int_a^b \Big(f(x)\Big)^2 dx \int_a^b \Big(g(x)\Big)^2 dx \qquad (36)$$

will be positive or 0. Hence

$$\left(\overline{\int}_a^b \left| f(x)g(x) \right| dx\right)^2 \leq \int_a^b \Big(f(x)\Big)^2 dx \int_a^b \Big(g(x)\Big)^2 dx \qquad (37)$$

This is a generalized form of the Schwartz inequality.[6] It may be used to demonstrate the following theorems:

(1) If $g(x)$ and every $\phi_n(x)$ is continuous, and

$$f(x) \sim \Sigma\, a_n \phi_n(x),$$

then

$$\int_a^b f(x)g(x)dx = \Sigma\, a_n \int_a^b \phi_n(x)g(x)dx \qquad (38)$$

Proof. Let

$$f(x) = \sum_1^n a_i \phi_i(x) + r_n(x).$$

Clearly

$$\overline{\int}_a^b f(x)g(x)dx \leq \sum_1^n a_i \int_a^b \phi_i(x)g(x)dx + \overline{\int}_a^b r_n(x)g(x)dx. \qquad (39)$$

and

$$\underline{\int}_a^b f(x)g(x)dx \geq \sum_1^n a_i \int_a^b \phi_i(x)g(x)dx + \underline{\int}_a^b r_n(x)g(x)dx \qquad (40)$$

Now

$$\left(\overline{\int}_a^b \left| r_n(x)g(x) \right| dx\right)^2 \leq \int_a^b \Big(r_n(x)\Big)^2 dx \int_a^b \Big(g(x)\Big)^2 dx, \qquad (41)$$

[6] *Cf.* Plancherel, loc. cit., p. 291.

and since $\int_a^b \left(r_n(x)\right)^2 dx$ approaches 0 as n increases, (38) is easily proved.

(2) We define $f(x)$ as above, and take the ϕ_n's as continuous. We let $K(x,y)$ be any continuous function of x and y. Then

$$\int_a^b dx \left(\int_a^b K(x,y)f(y)dy\right) = \int_a^b dy \left(\int_a^b K(x,y)f(y)dx\right). \tag{42}$$

Proof. Clearly

$$\int_a^b dx\left(\overline{\int}_a^b \left|K(x,y)r_n(y)\right| dy\right)$$

$$\leq \int_a^b dx \sqrt{\int_a^b \left(K(x,y)\right)^2 dy \int_a^b \left(r_n(y)\right)^2 dy}$$

$$\leq (b-a)^2 max\left|K\right| \sqrt{\int_a^b \left(r_n(y)\right)^2 dy} \tag{43}$$

and

$$\overline{\int}_a^b dy \left|\int_a^b K(x,y)r_n(y)dx\right| \leq (b-a)^2 max\left|K\right| \sqrt{\int_a^b \left(r_n(y)\right)^2 dy} \tag{44}$$

As f is the sum of r_n and a continuous function, the theorem follows as in (1).

Two functions $f(x)$ and $g(x)$ are said to be orthogonal if

$$\int_a^b f(x)g(x)dx = 0, \tag{45}$$

while a function $f(x)$ is said to be normal if

$$\int_a^b \left(f(x)\right)^2 dx = 1. \tag{46}$$

If $\{\psi_n\}$ is any denumerable set of continuous functions, it is possible to form a set ϕ_n such that

(1) every ϕ_n is linearly dependent on a finite number of ψ_n's;

(2) every ψ_n is linearly dependent on a finite number of ϕ_n's;

(3) the ϕ_n's form a normal, mutually orthogonal set.[6]

[6] Cf. Goursat, Cours d'analyse, Vol. 3, p. 391.

It is easily demonstrated that whenever $\{\phi_n\}$ is a normal orthogonal set of continuous functions and $f(x)$ is a continuous function,

$$g(x) \sim \Sigma \left(\int_a^b f(x)\phi_n(x)dx \right) \phi_n(x) \tag{47}$$

converges in the mean, and that

$$\int_a^b \Big(g(x) \Big)^2 dx \leq \int_a^b \Big(f(x) \Big)^2 dx \tag{48}$$[7]

Clearly $f(x)-g(x)$ will be orthogonal to every $\phi_n(x)$, and if $\{\phi_n\}$ is formed as above by normalizing a set $\{\psi_n\}$, $f(x)-g(x)$ will be orthogonal to every $\psi_n(x)$.

A set of functions is closed if there is no function of summable square orthogonal to every member of the set, aside from functions equivalent to 0. Normalization leaves invariant properties of closure. If $\{\phi_n\}$ is a normal orthogonal set of continuous functions and if $\{f_n\}$ is a closed set of continuous functions and

$$F_n(x) \sim f_n(x) - \Sigma \Big(\int_a^b f_n(x)\, \phi_i(x)dx \Big) \phi_i(x) \tag{49}$$

then if every $F_n(x)$ is equivalent to 0, $\{\phi_n\}$ is closed. For let $h(x)$, a function of summable square, be orthogonal to every $\phi_n(x)$. Then if we write $r_m(x)$ for $\sum_{m+1}^{\infty} \Big(\int_a^b f_n(x)\, \phi_i(x)dx \Big) \phi_i(x)$, then by the generalized Schwartz inequality, since

$$\begin{aligned} \overline{\int}_a^b f_n(x)\, h(x)dx &= \overline{\int}_a^b r_m(x)\, h(x)dx \\ &\leq \sqrt{\int_a^b \Big(r_m(x) \Big)^2 dx \int_a^b \Big(h(x) \Big)^2 dx} \end{aligned} \tag{50}$$

and since a similar relation holds for the lower integral, we have

$$\int_a^b f_n(x)h(x)dx = 0 \tag{51}$$

Hence $h(x)$ will be orthogonal to every $f_n(x)$.

If $\{\phi_n\}$ is a closed normal orthogonal set of continuous

[7] Ibid., pp. 444, 477.

functions and $f(x)$ is a summable function of summable square,

$$f(x) \sim \Sigma \left(\cdot \int_a^b \phi_n(x) f(x) dx \right) \phi_n(x) \tag{52}$$[8]

In the following sections of this paper, the results of this section will, in general, be assumed without explicit reference.

Verification of (24) when n is infinite. Let $i_1(x), i_2(x), \ldots, i_n(x), \ldots$ be any closed linearly independent set of continuous functions. Let $K(x,y)$[9] and $s(y)$ be continuous. Let a_{pq}, A_{pq}, a_n, a'_n, and b_n be defined as in paragraph 2. If no expression of the form A_{pp} vanishes, the a_n's and a_n''s will form a closed set, since the i_n's will be linear functions of a finite number of the a_n's or a_n''s. Let the series (24) converge in the mean to $r(x)$, and let $t(x)$ be a solution of (1). Then by (38)

$$a_n \cdot T \cdot (r-t) = \frac{(a_n \cdot T \cdot a_n')\, a_n \cdot s}{a_n \cdot T \cdot a_n'} - a_n \cdot T \cdot t = 0. \tag{53}$$

Since the a_n's form a closed set,

$$r(x) - t(x) - \lambda \int_a^b K(x,y) \left(r(y) - t(y) \right) dy \sim 0. \tag{54}$$

That is,

$$r(x) - t(x) \sim \lambda \int_a^b K(x,y) \left(r(y) - t(y) \right) dy \tag{55}$$

Since K is continuous, it is easy to prove that

$$\lambda \int_a^b K(x,y) \left(r(y) - t(y) \right) dy$$

is continuous. For by Schwartz' inequality

$$\left[\int_a^b \Delta_x K(x,y) \left(r(y) - t(y) \right) dy \right]^2 \tag{56}$$
$$\leq \int_a^b \left[\Delta_x K(x,y) \right]^2 dy \int_a^b \left[r(y) - t(y) \right]^2 dy$$

Hence there is a continuous function equivalent to $r(y) - t(y)$. Substituting this function in (55), we get an equality instead of an equivalence.

[8] Ibid., p. 445.

[9] The results of this paper remain valid, as is readily shown, when K is almost everywhere continuous (Goursat, p. 342.)

Now, if λ is not a characteristic number, (3) has no solution that is not identically 0. Hence

$$r(x)-t(x) \sim 0 \tag{57}$$

That is, the series in (24) converges in the mean to $t(x)$. It follows *a fortiori* that if the series (24) converges uniformly, it converges to a solution of (1).

7. **The Fredholm equation with iterated kernel.** From the Fredholm equation (1) we may derive the equation

$$\begin{aligned} s'(x) &= s(x) - \lambda \int_a^b K(y,x)s(y)dy \\ &= r(x) - \lambda \int_a^b K(x,y)r(y)dy - \lambda \int_a^b K(y,x)r(y)dy \\ &\quad + \lambda^2 \int_a^b \left\{ \int_a^b K(z,x)K(z,y)dz \right\} r(y)dy \qquad (58) \\ &= r(x) + \int_a^b \left\{ \lambda^2 \int_a^b K(z,x)K(z,y)dz - \lambda K(x,y) - \lambda K(y,x) \right\} r(y)dy \\ &= r(x) + \int_a^b Q(x,y)r(y)dy \end{aligned}$$

Clearly every solution of (1) will be a solution of (58), and if (58) is not singular and (1) has a solution, the solution of (58) must satisfy (1). Now, suppose that (1) is not singular, and let its solution be

$$s(x) - \int_a^b s(y)\, K'(x,y;\lambda)dy = r(x) \tag{59}$$

Then the homogeneous equation

$$r(x) + \int_a^b Q(x,y)r(y)dy = 0 \tag{60}$$

has no solution, for operating on both sides of (60) by the transformation which turns $u(x)$ into

$$u(x) - \int_a^b u(y)K'(x,y;\lambda)dy$$

we get

$$r(x) - \lambda \int_a^b r(y)K(y,x)dy = 0, \tag{61}$$

which is impossible, as (1) is not singular. Hence in the non-singular case the solution of (1) may be reduced to that of (58).

$Q(x, y)$ is clearly symmetrical, so that a biconjoint set of functions pertaining to (58) may sometimes be reduced to a single sequence, $a_1(x), a_2(x), \ldots, a_n(x), \ldots$, which we shall term a conjoint set with respect to (58). If we write

$$\phi_n(x) = a_n(x) - \lambda \int_a^b K(x,y) a_n(y) dy, \tag{62}$$

it may be seen without any difficulty that the functions $\phi_n(x)$ form an orthogonal set.

If we define a_{pq} and A_{pq} after a fashion analogous to that of paragraph 2, it may be seen without difficulty that

$$a_{qp} = a_{pq} = \int_a^b \left\{ i_p(x) - \lambda \int_a^b K(x,y) i_p(y) dy \right\} \left\{ i_q(x) - \lambda \int_a^b K(x,y) i_q(y) dy \right\} dx, \tag{63}$$

and

$$\begin{vmatrix} a_{11}, & a_{21}, & a_{31}, & \ldots, & a_{(n-1)1} \\ a_{21}, & a_{22}, & a_{32}, & \ldots, & a_{(n-1)2} \\ a_{31}, & a_{32}, & a_{33}, & \ldots, & a_{(n-1)3} \\ \cdot & \cdot & \cdot & \ldots, & \cdot \\ \cdot & \cdot & \cdot & \ldots, & \cdot \\ a_{(n-1)1}, & a_{(n-1)2}, & a_{(n-1)3}, & \ldots, & a_{(n-1)(n-1)} \end{vmatrix} = A_{nn} \tag{64}$$

If $A_{nn} = 0$, there is a linear dependence among the quantities

$$a_{k1} i_1(x) + a_{k2} i_2(x) + \ldots + a_{k(n-1)}\, i_{n-1}(x) = j_k(x)$$

That is, there are quantities $m_1, m_2, \ldots, m_{n-1}$, not all identically 0, such that

$$\sum m_k\, j_k(x) = 0 \tag{65}$$

Hence either there is a linear dependence among the i'_ks, or else every expression of the form

$$\sum_k m_k\, a_{kl}$$

vanishes. Now write

$$f(x) = \sum_k m_k\, i_k(x). \tag{66}$$

It follows from the definition of f that

$$\int_a^b \left\{ f(x) - \lambda \int_a^b K(x,y) f(y) dy \right\}^2 dx = 0 \tag{67}$$

Hence if the i's are continuous, we have

$$f(x) - \lambda \int_a^b K(x,y) f(y) dy = 0. \tag{68}$$

We thus have (3) satisfied by a function not identically 0, as the m_k's do not all vanish and the i_k's are linearly independent. This contradicts our hypothesis as to the non-singularity of (1). Hence if there is no linear dependence among the i_k's, the process of building up $r(x)$ in accordance with formula (24) offers no difficulties. It may readily be seen that because of the symmetry of $Q(x,y)$, $a_n(x)$ and $a_n'(x)$ will coincide and the set $\{a_n(x)\}$ will be conjoint.

Let us then start with the closed, linearly independent set of continuous functions $\{i_n\}$, and let us suppose (1) to be non-singular. Let us form in the manner just indicated the set of functions $\{a_n\}$, constituting linear combinations of the i_n's, and conjoint with respect to (58). Let us determine as above the orthogonal set $\{\phi_n\}$ of transforms of $\{a_n\}$. Clearly the set $\{a_n\}$ will be closed. It immediately results from this that the set $\{\phi_n\}$ will be closed. Otherwise there is some function $f(x)$ expressible by a series convergent in the mean of continuous functions, and orthogonal to every $\phi_n(x)$. Then

$$\int_a^b a_n(x) \left\{ f(x) - \lambda \int_a^b K(y,x) f(y) dy \right\} dx = 0. \tag{69}$$

Hence as in (54)–(57),

$$f(x) \sim 0. \tag{70}$$

If (1) is not singular and the series $\Sigma c_n \phi_n(x)$ converges in the mean to $\Phi(x)$, then we shall show that

$$\Sigma c_n a_n(x) \sim \Psi(x) = \Phi(x) - \int_a^b \Phi(y) K'(x,y;\lambda) dy. \tag{71}$$

Let us write

$$\Xi_n(x) = \Phi(x) - \sum_1^n c_i \phi_i(x)$$

and

$$H_n(x) = \Psi(x) - \sum_1^n c_i a_i(x).$$

We have

$$H_n(x) = \Xi_n(x) - \int_a^b \Xi_n(y)\, K'(x, y; \lambda)\, dy \tag{72}$$

and

$$\lim_{n \to \infty} \int_a^b \Big(\Xi_n(x) \Big)^2 dx = 0. \tag{73}$$

Now, by (37)

$$\begin{aligned}
\int_a^b \big(H_n(x)\big)^2 dx &= \int_a^b \Big(\Xi_n(x) \Big)^2 dx \\
&\quad - 2 \int_a^b \Xi_n(x) \left\{ \int_a^b \Xi_n(y) K'(x,y;\lambda) dy \right\} dx \\
&\quad + \int_a^b \left\{ \int_a^b \Xi(y) K'(x,y;\lambda)\, dy \right\}^2 dx \\
&\leq \int_a^b \Big(\Xi_n(x) \Big)^2 dx + 2 \int_a^b \Big| \Xi_n(x) \Big| \sqrt{\int_a^b \Big(\Xi_n(y) \Big)^2 dy \int_a^b (K')^2 dy}\, dx \\
&\quad + \int_a^b \Big(\int_a^b \Big(\Xi(y) \Big)^2 dy \int_a^b (K')^2 dy \Big) dx \\
&\leq \int_a^b \Big(\Xi_n(x) \Big)^2 dx \Big[1 + \sqrt{(b-a)\, max\, (K')^2} \Big]^2
\end{aligned} \tag{74}$$

Hence $\int_a^b \big(H_n(x)\big)^2 dx$ approaches 0 with $\int_a^b \Big(\Xi_n(x) \Big)^2 dx$.

Therefore $\Sigma c_n a_n(x)$ converges in the mean to $\Phi(x)$.

Now, by (52),

$$s(x) \sim \Sigma \phi_n(x) \frac{\int_a^b s(x)\, \phi_n(x)\, dx}{\int_a^b \big(\phi_n(x)\big)^2 dx}. \tag{75}$$

Hence by the results of the last paragraph,

$$r(x) \sim \Sigma\, a_n(x) \frac{\int_a^b s(x)\,\phi_n(x)\,dx}{\int_a^b \left(\phi_n(x)\right)^2 dx}. \tag{76}$$

We have thus obtained for the Fredholm equation with continuous kernel a solution that always converges in the mean in the non-singular case. It is easily verified that this answer may be obtained from (58) in precisely the same manner that (24) is obtained from (1).

8. **The law of inertia of quadratic forms.** Let equation (1) have a symmetric kernel, and let $\{\phi_i\}$ and $\{\psi_i\}$ be two sets of continuous functions each conjoint with respect to (1). Let it be possible to expand every $\phi_i(x)$ in a uniformly convergent series of $\psi_n(x)$'s, and *vice versa*. Let no ϕ_i .T. ϕ_i nor ψ_i .T. ψ_i vanish, and let the first m $\phi_i \cdot \mathrm{T} \cdot \phi_i$'s and the first n $\psi_i \cdot \mathrm{T} \cdot \psi_i$'s be negative, and no others. Then $m = n$.

This may be established as follows: let us write

$$\theta_i(x) = \sum_{j=1}^{m} \frac{\psi_i \,.\mathrm{T}.\, \phi_j}{\phi_j \,.\mathrm{T}.\, \phi_j}\, \phi_j(x) \quad [i = 1, \ldots, n] \tag{77}$$

Let us suppose that n is larger than m. Then it will be possible to determine $a_1, \ldots, a_n$ not all zero in such a manner that

$$\sum_1^n a_i \theta_i(x) \equiv 0. \tag{78}$$

Let us write

$$f(x) = \sum_1^n a_i \psi_i(x). \tag{79}$$

Expanding $f(x)$ in terms of the ϕ_i's we get

$$f(x) = \sum_{m+1}^{\infty} b_i \phi_i(x) \tag{80}$$

Consider f.T.f. By (79) we have

$$f \,.\mathrm{T}.\, f = \sum_1^n a_i^2\, \psi_i \,.\mathrm{T}.\, \psi < 0, \tag{81}$$

while by (80) we have

$$f.\mathrm{T}.f = \sum_{m+1}^{\infty} b_i^2 \phi_i . \mathrm{T} . \phi_i \geq 0. \tag{82}$$

As these are inconsistent, we see that n cannot be larger than m. Similarly n cannot be less than m. Hence they must be equal.

Now, it is readily shown that the normalized characteristic functions [solutions of (3)] form a conjoint set. Let $\{\phi_n\}$ be this set. Then if λ_i is the characteristic number belonging to ϕ_i,

$$\phi_i . \mathrm{T} . \phi_i = \int_a^b \phi_i(x) \left[\phi_i(x) - \lambda \int_a^b \mathrm{K}(x,y)\, \phi_i(y)\, dy \right] dx$$

$$= \int_a^b \phi_i(x) \left[\frac{\lambda}{\lambda_i} \left\{ \phi_i(x) - \lambda_i \int_a^b \mathrm{K}(x,y)\phi_i(y)dy \right\} + (1-\frac{\lambda}{\lambda_i})\phi_i(x) \right] dx$$

$$= 1 - \frac{\lambda}{\lambda_i}. \tag{83}$$

It follows from the fact that the characteristic numbers are the zeros of an entire function[10] and hence have no finite cluster-points, that only a finite number of the quantities $1-\dfrac{\lambda}{\lambda_i}$ can be negative. This number is equal to the number of characteristic numbers lying between 0 and λ.

An immediate result is the following: if $\{a_n\}$ is the set formed as in paragraph 2 by rendering conjoint a set $\{i_n\}$ and if every $i_n(x)$ can be expressed as a uniformly convergent series of $\phi_n(x)$'s, and *vice versa*, then whenever λ passes through a characteristic value, some $a_n . T . a_n$ changes sign. Now, every $a_n . T . a_n$ is of the form $A_{nn}A_{(n+1)(n+1)}$, and is a polynominal in λ. Hence all the characteristic values are roots of these polynomials. Among the denumerable set of these roots there may, it is true, be quantities not characteristic values. However, the fact that all the characteristic values are contained among these roots may be made the basis of a practical method of treating the homogeneous integral equation.

[10] Goursat, pp. 371, 380.

9. **The solution of the homogeneous integral equation.** Let λ assume a real characteristic value in (3). Let $\{i_n(x)\}$ be any set of functions, closed, continuous, and linearly independent. From these the set of functions

$$f_n(x) = i_n(x) - \lambda \int_a^b K(y,x) i_n(y) dy \tag{84}$$

may be formed. This set will not be closed, for every function belonging to the set will be orthogonal to every characteristic function belonging to the particular value assumed by λ.

Let us form the functions $g_n(x)$ in accordance with (27). Let $\{h_n\}$ be any closed set of continuous functions, and let

$$l_i(x) \frown h_i(x) - \Sigma g_n(x) \frac{\int_a^b g_n(x) h_i(x) dx}{\int_a^b \left(g_n(x) \right)^2 dx} \tag{85}$$

The existence of $l_i(x)$ is guaranteed by (47). As is obvious,

$$\int_a^b l_i(x) g_n(x) = 0. \tag{86}$$

Hence $l_i(x)$ is orthogonal to every $f_n(x)$, whence

$$\int_a^b i_n(x) \left\{ l_i(x) - \lambda \int_a^b \mathrm{K}(x,y) l_i(y) dy \right\} dx = 0 \tag{87}$$

As the i_n's form a closed set,

$$l_i(x) - \lambda \int_a^b \mathrm{K}(x,y) l_i(y) dy \frown 0. \tag{88}$$

As was shown in the case of (54), there is then a continuous function $m(x)$ equivalent to $l_i(x)$ such that

$$m(x) - \lambda \int_a^b \mathrm{K}(x,y) m(y) dy = 0. \tag{89}$$

Hence $l_i(x)$ is equivalent to a characteristic function pertaining to λ. There are thus only a finite number of non-equivalent l_i's.

It results from (85) and the closure of the h_i's that every function orthogonal to the l_i's and to the g_n's is equivalent to 0. Now, let $L(x)$ be any continuous function orthogonal to all the

g_n's. Normalize the finite set of l_i's, forming $p_1(x), \ldots, p_m(x)$, which shall be taken as continuous. Construct

$$M(x) = \sum_1^m p_i(x) \int_a^b p_i(x) L(x) dx - L(x). \tag{90}$$

$M(x)$ will be orthogonal to all the p_i's, and hence will vanish. Thus every characteristic function pertaining to λ will be linearly dependent on the p_i's.

10. **The verification of (31).** Let (1) be non-singular and let

$$s_i(x) = r_i(x) - \lambda \int_a^b K(x,y) r_i(y) dy$$

exist and be orthogonal to every

$$\beta_n(x) = \begin{vmatrix} i_n(x) & , & i_{n+1}(x) \\ \int_a^b i_n(x) s(x) dx, & & \int_a^b i_{n+1}(x) s(x) dx \end{vmatrix}$$

Then, as is easiiy verified, there is some quantity v_i, such that $s_i(x) - v_i s(x)$ is orthogonal to every $i_n(x)$, if the i_n's form a closed set. It follows that

$$s_i(x) - v_i s(x) \backsim 0 \tag{91}$$

Hence, unless $s_i(x) \backsim 0$

$$\frac{r_i(x)}{v_i} - \lambda \int_a^b K(x,y) \frac{r_i(y)}{v_i} dy \backsim s(x) \tag{92}$$

It follows by a reasoning of which we have repeatedly made use that $\dfrac{r_i(x)}{v_i}$ is equivalent to a solution of (1).

Now, let the i_n's be continuous and form the functions

$$f_n(x) = \beta_n(x) - \lambda \int_a^b K(y,x) \beta_n(y) dy \tag{93}$$

These will likewise be continuous. Normalize the set $\{f_n\}$, obtaining the set $\{g_n\}$. Let $\{h_n\}$ be a closed set of continuous functions, and form the functions

$$r_n(x) \sim h_n(x) - \Sigma g_m(x) \frac{\int_a^b g_m(x) h_n(x) dx}{\int_a^b \left(g_m(x) \right)^2 dx} \tag{94}$$

These functions will be orthogonal to every $f_n(x)$, so that

$$s_n(x) = r_n(x) - \lambda \int_a^b K(x,y) r_n(y) dy$$

will be orthogonal to every $\beta_n(x)$.

As we have already repeatedly seen, if $s_n(x) \sim 0$, then $r_n(x) \sim 0$. Hence if every $s_n(x)$ is equivalent to 0, any function orthogonal to all the $g_m(x)$'s will, by (94), be orthogonal to every $h_n(x)$. Now, if $r(x)$ is a solution of (1), we have

$$\int_a^b r(x) \beta_n(x) - \lambda \int_a^b \int_a^b K(x,y) \beta_n(y) r(x) dx\, dy = 0 \tag{95}$$

Hence $r(x)$ is orthogonal to every $f_n(x)$, and hence to every $g_n(x)$ and $h_n(x)$, so that the $h_n(x)$'s do not form a closed set; which contradicts our assumptions. Therefore at least one of the functions $r_n(x)$ gives us, except for a constant factor, a solution of (1).

ON THE GEOMETRY OF MOTION IN CURVED N-SPACE

By JOSEPH LIPKA

1. **Introduction.** If we consider the motion of a particle in a general curved space of n dimensions under *any positional field of force*, we find that the possible paths or trajectories are ∞^{2n-1} in number, such that ∞^n trajectories pass through a given point, ∞^1 through a given point in a given direction, and a unique trajectory passes through a given point in a given direction with a given initial speed. Again, if we consider the motion of a particle in a general curved space of n dimensions in a *conservative field of force*, and for a given constant of energy, the minimizing of a certain integral defines a system of ∞^{2n-2} curves, termed a *natural system*, a unique curve passing through a given point in a given direction. Of these natural systems, the trajectories under the principle of least action, the brachistochrones, the catenaries, and the velocity curves are the most interesting special cases. The ∞^1 natural systems for all possible values of the energy constant will then consist of ∞^{2n-1} curves, termed a "q" system, a unique curve passing through a given point in a given direction with a given initial speed.

Complete geometric characterization of dynamical trajectories for any positional field of force in flat or euclidean spaces of two and three dimensions have been given by E. Kasner,[1] for a flat space of n dimensions by L. M. Kells,[2] and for a surface or curved space of two dimensions by the author.[3] Complete geometric characterization of "q" systems have been given for the plane (two dimensions) by E. Kasner,[4] and for a surface (two dimensions) by the author.[3]

[1] *The Trajectories of Dynamics*, Trans. Am. Math. Soc., Vol. 7 (1906), pp. 401-424; and *Dynamical Trajectories; the Motion of a Particle in an Arbitrary Field of Force*, Trans. Am. Math. Soc., Vol. 8 (1907), pp. 135-158.

[2] *Complete Characterization of Dynamical Trajectories in n Space*, Columbia University Dissertation, Lancaster, Pa., 1913.

[3] *Motion on a Surface for any Positional Field of Force*, Proc. Nat. Acad. Arts and Sciences, Vol. 6 (1920), No. 10, pp. 621-624, and Proc. Am. Acad. Arts and Sciences, Vol. 56 (1921), No. 4, pp. 155-182.

[4] *Differential Geometric Aspects of Dynamics*, The Princeton Colloquium Lectures on Mathematics, Am. Math. Soc., p. 94.

It is the purpose of this paper to derive a number of interesting geometric properties of the system of dynamical trajectories for any positional field of force, and of "q" systems, in a curved space of n dimensions. In such a space, the element of length ds is defined by the quadratic differential form

$$ds^2 = \sum_{ij}^{1 \ldots n} a_{ij} dx_i dx_j,$$

where the a's are functions of the coördinates $x_1, x_2, \ldots, x_n$.

2. **The Equations of Dynamical Trajectories for any Positional Field of Force.** Let us consider the motion of a particle in a curved n-space under any positional forces. The element of length in such a space is given by[5]

$$ds^2 = \sum_{ij} a_{ij}\, dx_i\, dx_j. \tag{1}$$

The motion is defined by the Lagrangian equations

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{x}_l}\right) - \frac{\partial T}{\partial x_l} = \phi_l \qquad (l = 1, 2, \ldots, n), \tag{2}$$

where the kinetic energy is

$$T = \tfrac{1}{2} \sum_{ij} a_{ij} \dot{x}_i \dot{x}_j, \tag{3}$$

and the ϕ's are the components of force given as functions of the coördinates $x_1, x_2, \ldots, x_n$. Expanding (2) we get

$$\sum_j a_{jl} \ddot{x}_j + \sum_{ij} [ij,l]\, \dot{x}_i\, \dot{x}_j = \phi_l \qquad (l = 1, 2, \ldots, n), \tag{4}$$

where we have employed the Christoffel symbol of the first kind

$$[ij,l] = \tfrac{1}{2}\left(\frac{\partial a_{il}}{\partial x_j} + \frac{\partial a_{jl}}{\partial x_i} - \frac{\partial a_{ij}}{\partial x_l}\right). \tag{5}$$

If we designate by A_{kl} the result of dividing the minor of a_{kl}

[5] Throughout, the summations are to extend from 1 to n for the indicated subscripts, unless otherwise specified. We shall use primes to refer to total derivatives with respect to s, thus $x' = \frac{dx}{ds}$, $x'' = \frac{d^2x}{ds^2}$, ..., and dots to refer to total derivatives with respect to t, thus $\dot{x} = \frac{dx}{dt}$, $\ddot{x} = \frac{d^2x}{dt^2}$, ...

in the determinant of the a's by the determinant $|a|$ itself, we have the identities

$$\sum_l a_{jl} A_{kl} = \begin{cases} 0, \text{ if } j \neq k \\ 1, \text{ if } j = k \end{cases} \tag{6}$$

Now, multiplying equations (4) by A_{kl}, summing with respect to l and employing the Christoffel symbol of the second kind

$$\left\{ ij,k \right\} = \sum_l A_{kl} \ [ij,l], \text{ and hence, } [ij,l] = \sum_k a_{kl} \left\{ ij,k \right\}, \tag{7}$$

we get

$$\ddot{x}_k + \sum_{ij} \left\{ ij,k \right\} \dot{x}_i \dot{x}_j = \sum_l A_{kl} \phi_l \quad (k = 1, 2, \ldots, n). \tag{8}$$

These equations give the components of acceleration along the curve as functions of the coördinates and the components of velocity. We may also get the acceleration along the path by differentiating the velocity given by

$$\dot{s}^2 = \sum_{ij} a_{ij} \dot{x}_i \dot{x}_j ;$$

thus,

$$\begin{aligned} \dot{s}\ddot{s} &= \sum_{ij} a_{ij} \dot{x}_i \ddot{x}_j + \tfrac{1}{2} \sum_{ijr} \frac{\partial a_{ij}}{\partial x_r} \dot{x}_i \dot{x}_j \dot{x}_r \qquad (9) \\ &= \sum_{ij} a_{ij} \dot{x}_i \Big(\sum_l A_{jl} \phi_l - \sum_{\alpha\beta} \left\{ \alpha\beta,j \right\} \dot{x}_\alpha \dot{x}_\beta \Big) + \tfrac{1}{2} \sum_{ijr} \frac{\partial a_{ij}}{\partial x_r} \dot{x}_i \dot{x}_j \dot{x}_r \\ &= \sum_l \dot{x}_l \phi_l - \sum_{i\alpha\beta} [\alpha\beta, i] \dot{x}_i \dot{x}_\alpha \dot{x}_\beta + \tfrac{1}{2} \sum_{i\alpha\beta} \frac{\partial a_{i\alpha}}{\partial x_\beta} \dot{x}_i \dot{x}_\alpha \dot{x}_\beta \\ &= \sum_l \ddot{x}_l \phi_l . \end{aligned}$$

To derive the differential equations of the trajectories, we shall have to eliminate the time from equations (8). Using the arc length s as parameter along the curves, we evidently have

$$\sum_{ij} a_{ij} \, x'_i \, x'_j = 1, \tag{10}$$

$$x'_k = \frac{\dot{x}_k}{\dot{s}}, \quad x''_k = \frac{\dot{s}\ddot{x}_k - \dot{x}_k \ddot{s}}{\dot{s}^3} . \tag{11}$$

Introducing (8) and (9) into (11), we get

$$x''_k = \frac{1}{\dot{s}^2} \sum_l A_{kl} \phi_l - \sum_{ij} \left\{ ij,k \right\} x'_i \, x'_j - \frac{1}{\dot{s}^2} x'_k \sum_l \phi_l x'_l$$

or

$$x''_k + \sum_{ij} \left\{ ij,k \right\} x'_i x'_k = \frac{1}{s^2} \sum \phi_l (A_{kl} - x'_k x'_l) \quad (k=1, 2, \ldots, n). \tag{12}$$

From (12) we see that one set of equations free of the time are

$$\frac{\sum_l \phi_l (A_{1l} - x'_1 x'_l)}{x''_1 + \sum_{ij} \left\{ ij,1 \right\} x'_i x'_j} = \frac{\sum_l \phi_l (A_{2l} - x'_2 x'_l)}{x''_2 + \sum_{ij} \left\{ ij,2 \right\} x'_i x'_j} = \ldots\ldots$$

$$= \frac{\sum \phi_l (A_{nl} - x'_n x'_l)}{x''_n + \sum_{ij} \left\{ ij,n \right\} x'_i x'_j} \tag{13}$$

If we introduce the abbreviation

$$G_k = x''_k + \sum_{ij} \left\{ ij,k \right\} x'_i x'_j \qquad (k=1, 2, \ldots, n), \tag{14}$$

where

$$G_k = 0 \qquad (k=1, 2, \ldots, n) \tag{15}$$

are the differential equations of the system of geodesics in our space, equations (12) and (13) may be more simply written

$$\dot{s}^2 = \frac{1}{G_k} \sum_l \phi_l (A_{kl} - x'_k x'_l) \qquad (k=1, 2, \ldots, n), \tag{16}$$

$$\frac{1}{G_1} \sum_l \phi_l (A_{1l} - x'_1 x'_l) = \frac{1}{G_k} \sum_l \phi_l (A_{kl} - x'_k x'_l) \quad (k=2, 3, \ldots, n). \tag{17}$$

Of course, the $(n-1)$ equations (17) are not sufficient for the determination of our system of curves. We may get another set of equations free of the time by differentiating (16) with respect to s and using (9), thus getting

$$2G_k^2 \sum_l \phi_l x'_l = G_k \frac{d}{ds} \sum_l \phi_l (A_{kl} - x'_k x'_l) - G'_k \sum_l \phi_l (A_{kl} - x'_k x'_l),$$

or

$$G'_k \sum_l \phi_l (A_{kl} - x'_k x'_l) = G_k \left\{ \sum_{il} \left[\frac{\partial \phi_l}{\partial x_i} (A_{kl} - x'_k x'_l) - \phi_l \frac{\partial A_{kl}}{\partial x_i} \right] x'_i \right.$$

$$\left. - \sum_l \phi_l (x''_k x'_l + x''_l x'_k) - 2G_k^2 \sum_l \phi_l x'_l \right\} \quad (k=1, 2, \ldots, n), \tag{18}$$

where

$$G'_k = \frac{dG_k}{ds} = x'''_k + 2 \sum_{ij} \left\{ ij,k \right\} x'_i x''_j$$

$$+ \sum_{ijl} \frac{\partial}{\partial x_l} \left\{ ij,k \right\} x'_i x'_j x'_l \quad (k=1, 2, \ldots n) \tag{19}$$

Equations (18) are n differential equations of the third order. We need only one of these equations, say that one given by $k=1$, together with the $(n-1)$ equations (17) of the second order to determine our system of ∞^{2n-1} curves, for the others may evidently be derived by differentiation of equâtions (17). Thus, the dynamical trajectories in any positional field of force are completely defined by the $(n-1)$ differential equations (17) of the second order and any one of the equations (18) of the third order. Along these curves, the relation (10) holds, *i.e.*, the arc length is the parameter.

Thus, given a point $(x_1, x_2, \ldots, x_n)$ and a direction $(x'_1, x'_2, \ldots, x'_n)$ through this point, we may assign any value to the speed $\dot{s}$; then equations (16) will determine $(x''_1, x''_2, \ldots, x''_n)$ and equations (18) will determine $(x'''_1, x'''_2, \ldots, x'''_n)$ and all higher derivatives of the coördinates by differentiation, and so a unique trajectory is determined.

3. **Equations of " q " Systems.** Let us consider the extremals, connected with a variation problem of the form

$$\int_{s_0}^{s_1} F ds = \textit{minimum}, \tag{20}$$

where F is any point function, and ds is the element of length defined by (1). If we choose the arc length as the parameter along an extremal and apply the ordinary methods of the calculus of variation to (20), we find for the differential equation of the system

$$x''_k + \sum_{ij} \left\{ ij,k \right\} x'_i x'_j = \frac{1}{F} \sum_l \frac{\partial F}{\partial x_l} (A_{kl} - x'_k x'_l) \quad (k=1, 2, \ldots, n). \tag{21}$$

Equations (21) define a system of ∞^{2n-2} curves, termed a " *natural family* " of curves, one curve passing through each point in each direction through that point.[6]

[6] A complete geometric characterization of " natural families " of curves was given by the author in *Natural Families of Curves in a General Curved Space of n Dimensions*, Trans. Am. Math. Soc., Vol. 13 (1912), pp. 77-95. A different geometric characterization of these systems was given by the author in *Some Geometric Investigations on the General Problem of Dynamics*, Proc. Am. Acad. of Arts and Sciences, Vol. 55 (1920), pp. 283-322. For a study of these systems in a plane and ordinary 3-space, see Professor Kasner's Princeton Colloquium Lectures, Chapter II. Interesting generalizations of these systems in a plane and on a surface were given by K. Ogura in the *Tôhoku Math. Journal*, Vol. 8 (1915), pp. 93-107 and pp. 213-217.

Now, if, in our space, we have a conservative field of force defined by the work function (negative potential) W, and a given constant of energy h, and we replace F by $(W+h)^{\frac{1}{2q}}$, then the extremals defined by (20) represent the *trajectories determined according to the principal of least action*, when $q=1$, the trajectories determined under the principle of least time, *i.e.*, *brachistochrones*, when $q=-1$, and the forms of equilibrium of a homogeneous, flexible, inextensible string, *i.e.*, *general catenaries*, when $q=\frac{1}{2}$. Equations (21) become

$$x''_k+\sum_{ij}\left\{ij,k\right\}x'_ix'_j=\frac{1}{2q(W+h)}\sum_l\frac{\partial W}{\partial x_l}(A_{kl}-x'_kx'_l)(k=1,2,\ldots n). \tag{22}$$

We thus have a natural family of ∞^{2n-2} curves for each value of the constant of energy h. The totality of motions for all initial conditions giving ∞^{2n-1} curves will be found by eliminating h from equations (22). If in (22) we replace $\dfrac{\partial W}{\partial x_l}$ by ϕ_l, and introduce the velocity

$$\dot{s}^2=2(W+h), \tag{23}$$

these equations take the form

$$q\dot{s}^2=\frac{1}{G_k}\sum_l\phi_l(A_{kl}-x'_kx'_l)\quad(k=1,2,\ldots,n). \tag{24}$$

We thus get a set of $(n-1)$ differential equations of the second order free of h,

$$\frac{1}{G_1}\sum_l\phi_l(A_{1l}-x'_1x'_l)=\frac{1}{G_k}\sum_l\phi_l(A_{kl}-x'_kx'_l)\quad(k=2,3,\ldots,n.) \tag{25}$$

these have the same form as equations (17), and are also independent of the value of q. Differentiating (24) with respect to s, and using

$$\left\{\begin{aligned}&2\dot{s}\ddot{s}=2\dot{W}=2\sum_l\frac{\partial W}{\partial x_l}\dot{x}_l=2\sum_l\phi_l\dot{x}_l\\&\ddot{s}=\sum_l\phi_lx'_l,\end{aligned}\right. \tag{26}$$

we get the desired $(n\text{-}1)$ equations of the third order

$$G'_k \sum_l \phi_l (A_{kl} - x'_k x'_l) = G_k \left\{ \sum_{il} \left[\frac{\partial \phi_l}{\partial x_i} (A_{kl} - x'_k x'_l) - \phi_l \frac{\partial A_{kl}}{\partial x_i} \right] x'_i \right.$$
$$\left. - \sum_l \phi_l (x''_k x'_l + x''_l x'_k) - 2q G^2_k \sum_l \phi_l x'_l \right\} \quad (k = 1, 2, \ldots, n). \tag{27}$$

A system of curves defined by equations (25) and any one of equations (27) will be termed a "q" system. If in (27) we think of the ϕ's as the components of an arbitrary force instead of as the components of a conservative force, and let $q=1$, we shall have equations (18). Thus we may enlarge our "q" systems by including systems defined by (25) and (27) where the ϕ's are arbitrary functions instead of the partial derivatives of one function W. If the force is not conservative we may speak of pseudo-brachistochrones and pseudo-catenaries.

There is another interesting system of curves which may be included under "q" systems, *viz.*, *velocity curves*. If in equations (12) we replace the variable speed s along a trajectory by a constant c, these will be the differential equations of ∞^{2n-2} curves, termed a velocity system. Thus, a curve is a velocity curve corresponding to the speed c, if a particle starting from a point of such a curve and in the direction of the curve with a speed c, describes a trajectory osculating the curve.[7] The complete system of ∞^{2n-1} velocity curves is found by eliminating c from equations (12). We evidently obtain equations (25) and (27), with $q=0$.

We shall now derive some of the geometric properties of a *general "q" system, defined by equations* (25) *and any one of equations* (27), together with the relation (10), where the ϕ's are arbitrary point functions and q may have any value including zero.

It is immediately evident that $G_k=0$ $(k=1, 2, \ldots, n)$ satisfy these equations, so that the system of ∞^{2n-2} geodesics in our space form part of every "q" system. Indeed, from (24) we note that the speed of a particle describing a geodesic is infinite.

[7] See the author's *Note on Velocity Systems in a Curved Space of n Dimensions*, Bull. Am. Math. Soc., Vol. 27 (1920), pp. 71-77.

Further, the ϕ's are the components of the force in the directions of the parameter curves, *i.e.*, $\phi_l\,dx_l$. is the work done by the force in the displacement which corresponds to a change of x_l from x_l to x_l+dx_l, the other coördinates being unaltered. If the direction of the force vector is given by $x'_l = \eta_l$ ($l=1, 2, \ldots, n$) and K represents the magnitude of the force vector, then

$$\phi_l = K\cos(K,x_l) = K\sum_j a_{jl}\eta_j \qquad (l=1, 2, \ldots, n).$$

Multiplying by A_{il} and summing with respect to l, we obtain

$$\sum_l A_{il}\,\phi_l = K\eta_i \qquad (i=1, 2, \ldots, n).$$

Hence we have for the direction of the force vector

$$dx_1 : dx_2 : \ldots : dx_n = \sum_l A_{1l}\,\phi_l : \sum_l A_{2l}\,\phi_l : \ldots : \sum_l \phi_l\,A_{nl}, \quad (28)$$

which we shall designate briefly by

$$\sum_l A_{kl}\,\phi_l \quad (k=1, 2, \ldots, n). \qquad (29)$$

Equations (28) are evidently the differential equations of the lines of force. In the case of conservative forces, the condition of orthogonality of the direction (29) and any direction dx_i ($i=1, 2, \ldots, n$),

$$\sum_{ik} a_{ik}\left(\sum_l A_{kl}\phi_l\right)dx_i = \sum_{ik} a_{ik}\left(\sum_l A_{kl}\frac{\partial W}{\partial x_l}\right)dx_i = \sum_l \frac{\partial W}{\partial x_l}\,dx_l = dW = 0$$

is fulfilled for the equipotential hypersurfaces $W=$constant, as it should be.

4. **Osculating Geodesic Surfaces.** At any point M_0 of a curve the tangent direction x'_k ($k=1, 2, \ldots, n$) and the direction of the principal geodesic normal[8] ξ_k($k=1, 2, \ldots, n$) determine a pencil of ∞^1 directions,

[8] If we draw the geodesic g (lying in the space) passing through the point M_0 in the same direction as the curve c and lay off on c and g equal infinitesimal arc lengths M_0M_1 and M_0M_2 respectively, then the geodesic curvature $1/\rho$ of c at M_0 is defined by $1/\rho = 2M_1M_2/(M_0M_1)^2$. The limiting position of the direction M_1M_2 defines the direction of the principal geodesic normal at M_0. This definition coincides with that of the ordinary curvature of a curve lying in a euclidean space. See Bianchi, *Geometria differenziale*, Vol. 1, pp. 363-364.

$$\zeta_k = \alpha x'_k + \beta \xi_k \qquad (k=1, 2, \ldots, n). \tag{30}$$

The pencil of ∞^1 geodesics passing through M_0 in this pencil of directions form a two dimensional spread called the osculating geodesic surface to the curve at M_0. Now

$$\xi_k = \rho G_k \qquad (k=1, 2, \ldots, n) \tag{31}$$

where G_k is defined by equation (14) and ρ is the radius of geodesic curvature. But for a curve of the "q" system we have by (24)

$$G_k = \frac{1}{qs^2} \sum_l \phi_l (A_{kl} - x'_k x'_l), \qquad (k=1, 2 \ldots, n),$$

hence (30) may be written

$$\zeta_k = x'_k \left(\alpha - \frac{\beta\rho}{qs^2} \sum_l \phi_l x'_l\right) + \frac{\beta\rho}{qs^2} \sum_l \phi_l A_{kl} \quad (k=1, 2, \ldots, n). \tag{32}$$

Now, if we choose

$$\frac{\alpha}{\beta} = \frac{\rho}{qs^2} \sum_l \phi_l x'_l,$$

which is the same for all values of the subscript k, we have

$$\zeta_k = \frac{\beta\rho}{qs^2} \sum_l \phi_l A_{kl} \qquad (k=1, 2, \ldots, n)$$

Thus, the osculating geodesic surface contains the direction $\sum_l \phi_l A_{kl}$ $(k=1, 2, \ldots, n)$ which, by (29) is the direction of the force vector.

The osculating geodesic surface at a point M_0 of a curve of a "q" system is therefore determined by the direction of the tangent line and the direction of the force vector. We may then state

Theorem 1. *The ∞^1 curves of a "q" system which pass through a given point in a given direction all have a common osculating geodesic surface.*

Further, since the direction of the force vector at a point is independent of the direction of the tangent line, all the osculating geodesic surfaces at a point must contain the direction of the

force vector, or the ∞^{n-1} osculating geodesic surfaces at a point form a bundle. Hence,

Theorem 2. *The ∞^{n-1} osculating geodesic surfaces of a "q" system which pass through a given point form a bundle of surfaces, i.e., they all contain a fixed direction, the direction of the force vector, through the point.*

Since, in the above proof, we have only used equations (24) or their equivalents (25) of the "q" system, the geometric properties expressed in the above theorems must belong to systems of curves other than "q" systems. It is of interest to find the most general system of ∞^{2n-1} curves which possess the above properties.

Let the direction fixed for each point be given by the arbitrary functions of the coördinates, ω_k $(k=1, 2, \ldots, n)$. Since the osculating geodesic surface given by (30) must contain this direction for all values of x'_k and ξ_k, we must have

$$\omega_k = \alpha x'_k \beta + \xi_k \qquad (k=1, 2, \ldots, n) \tag{33}$$

To eliminate α and β we multiply by $a_{kl}\, x'_l$ and sum with respect to k and l, thus

$$\sum_{kl} a_{kl}\, \omega_k\, x'_l = \alpha \sum_{kl} a_{kl}\, x'_k\, x'_l + \beta \sum_{kl} a_{kl}\, \xi_k\, x'_l$$

By (10) the coefficient of α is equal to 1, and since the tangent direction x' and the direction of the principal geodesic normal ξ are orthogonal, the coefficient of β is equal to 0, hence

$$\sum_{kl} a_{kl}\, \omega_k x'_l = \alpha \ .$$

Substituting this value of α into (33) and using (31), we have

$$\omega_k - x'_k \sum_{ij} a_{ij}\, \omega_i\, x'_j = \beta \rho G_k \quad (k=1, 2, \ldots, n),$$

or

$$\frac{1}{G_1}\left[\omega_1 - x'_1 \sum_{ij} a_{ij}\omega_i x'_j\right] = \frac{1}{G_k}\left[\omega_k - x'_k \sum_{ij} a_{ij}\omega_i x'_j\right] (k=2,3, \ldots, n). \tag{34}$$

Conversely, when conditions (34) are fulfilled, the curves have the required property. We note that there is no condition on the third derivatives of the coördinates. Hence,

Theorem 3. *The most general system of* ∞^{2n-1} *curves such that the* ∞^{n-1} *osculating geodesic surfaces at a point form a bundle, i.e., contain a fixed direction* $\omega_k (k=1, 2, \ldots, n)$ *through the point, are defined by differential equations of the form*

$$\left\{\begin{aligned} &\frac{1}{G_1}[\omega_1 - x'_1 \sum_{ij} a_{ij}\omega_i x'_j] = \frac{1}{G_k}[\omega_k - x'_k \sum_{ij} a_{ij}\omega_i x'_j], \ (k=2,3,\ldots,n) \\ &x'''_1 = f(x_1, \ldots, x_n, x'_1, \ldots, x'_n, x''_1, \ldots, x''_n), \end{aligned}\right. \tag{35}$$

containing n arbitrary functions $\omega_k (k=1, 2, \ldots, n)$ *of the x's and one arbitrary function of the x's, x"s, and x"'s.*

If we set $\omega_k = \sum_l A_{kl}\phi_l$, then

$$\sum_{ij} a_{ij}\,\omega_i\,x'_j = \sum_{ijl} a_{ij}\,A_{il}\,\phi_l\,x'_j = \sum_l \phi_l\,x'_l,$$

and equations (34) immediately reduce to equations (25).

5. **Hyperosculating Geodesic Surfaces.** Let us now inquire as to the number of curves of a "q" system which are hyperosculated by (have four-point contact with) their osculating geodesic surfaces. The author, on page 88 of the first paper, mentioned in Note (6), has derived the conditions that the osculating geodesic surface should hyperosculate any curve determined by $x_k, x'_k, x''_k, x'''_k, (k=1, 2, \ldots, n)$. These conditions are

$$\lambda_3 x'_k + \mu_3 G_k - \tfrac{1}{2}\sum_{\lambda\mu}\left\{\lambda\mu, k\right\} x'_\lambda G_\mu + \tfrac{1}{6}\sum_{\lambda\mu\nu}\Big(2\sum_h \left\{\lambda h, k\right\}\left\{\mu\nu, h\right\} - \frac{\partial}{\partial x_\nu}\left\{\lambda\mu, k\right\}\Big) x'_\lambda x'_\mu x'_\nu - \tfrac{1}{6}x'''_k = 0. \quad (k=1, 2, \ldots, n) \tag{36}$$

where λ_3 and μ_3 are parameters. By differentiation of

$$G_k = x''_k + \sum_{\lambda\mu}\left\{\lambda\mu, k\right\} x'_\lambda\, x'_\mu \qquad (k=1, 2, \ldots, n),$$

we find

$$x'''_k - \sum_{\lambda\mu\nu}\Big(2\sum_h \left\{\lambda h, k\right\}\left\{\mu\nu, h\right\} - \frac{\partial}{\partial x_\nu}\left\{\lambda\mu, k\right\} x'_\lambda\, x'_\mu\, x'_\nu = G'_k - 2\sum_{\lambda\mu}\left\{\lambda\mu, k\right\} x'_\lambda G_\mu,$$

and substituting this into (36) we obtain

$$\lambda_3 x'_k + \mu_3 G_k - \tfrac{1}{6}\sum_{\lambda\mu}\left\{\lambda\mu, k\right\} x'_\lambda G_\mu - \tfrac{1}{6}G'_k = 0 \ \ (k=1, 2, \ldots n), \tag{37}$$

If from these n equations we eliminate the parameters λ_2 and μ_2, and introduce the values of G_k and G'_k from equations (25) and (27), we get, after considerable reduction,

$$\left|\begin{array}{lll} x'_1 & \sum_l A_{1l}\phi_l & \sum_{l\lambda\mu}\{\lambda\mu,1\}A_{l\mu}\phi_l x'_\lambda + \sum_{l\lambda}\frac{\partial(\phi_l A_{1l})}{\partial x_\lambda}x'_\lambda \\ x'_2 & \sum_l A_{2l}\phi_l & \sum_{l\lambda\mu}\{\lambda\mu,2\}A_{l\mu}\phi_l x'_\lambda + \sum_{l\lambda}\frac{\partial(\phi_l A_{2l})}{\partial x_\lambda}x'_\lambda \\ x'_k & \sum_l A_{kl}\phi_l & \sum_{l\lambda\mu}\{\lambda\mu,k\}A_{l\mu}\phi_l x'_\lambda + \sum_{l\lambda}\frac{\partial(\phi_l A_{kl})}{\partial x_\lambda}x'_\lambda \end{array}\right| = 0 \quad (k=3, 4, \ldots, n) \tag{38}$$

These $(n-2)$ equations are $(n-2)$ conditions on the values of x'_k $(k=1, 2, \ldots, n)$ and thus pick ∞^1 directions through a given point in which the hyperosculating property holds. Further, since equations (38) do not involve x''_k $(k=1, 2, \ldots, n)$, the hyperosculating property holds for all the curves which pass through a point in these ∞^1 directions, and hence there are ∞^2 curves through a point which possess this property. Since equations (38) are quadratic homogeneous expressions in x'_k $(k=1, 2, \ldots, n)$, these ∞^1 directions through a point generate a cone (conical spread of two dimensions) of order 2^{n-2}. Since the quantity q does not enter these equations, this cone is the same for all "q" systems in a given field of force. We may now state

Theorem 4. *Of the ∞^n curves of a "q" system which pass through a point, there are ∞^2 which hyperosculate their respective osculating geodesic surfaces. The ∞^1 initial directions of these curves generate a cone (conical spread of two dimensions) of order 2^{n-2}, which is the same for all possible "q" systems in a given field of force.*[9]

We also note that equations (38) are satisfied if x'_k $(k=1, 2, \ldots, n)$ is proportional to $\sum_l A_{kl}\phi_l$ $(k=1, 2, \ldots, n)$. Since the latter direction is that of the force vector, we may state

Theorem 5. *The cone of Theorem* 4 *contains the direction of the force vector.*

[9] L. M. Kells in his dissertation mentioned in Note (2) erroneously states that in a euclidean n — space, there are ∞^{n-1} dynamical trajectories through a point which have hyperosculating planes, and that the lineal elements of these determine a quadric hypercone.

6. **Hyperosculating Geodesic Circles.**[10] Consider a point M_0 of a curve c belonging to a "q" system, and draw in its osculating geodesic surface σ at the point the geodesic circle j (curve of constant geodesic curvature, that of c at M_0) which osculates the curve c. At a point of c, and lying in σ, there is one and only one such curve j. The curve j may be called the osculating geodesic circle of c at M_0. Let us find the conditions that j should hyperosculate c. It is evident that the osculating geodesic surface must hyperosculate, *i.e.*, conditions (38) must hold, and in addition we must have

$$\frac{d\rho}{ds} = 0, \tag{39}$$

where ρ is the radius of geodesic curvature. Now, the geodesic curvature for any curve is given by [11]

$$\frac{1}{\rho^2} = \sum_{ij} A_{ij} G_i G_j , \tag{40}$$

and applying this to a curve of a "q" system we have by (24)

$$\frac{1}{\rho^2} = \frac{1}{q^2 \dot{s}^4} \sum_{ij} a_{ij} \left[\sum_l \phi_l (A_{il} - x'_i x'_l) \right] \left[\sum_m \phi_m (A_{jm} - x'_j x'_m) \right] \tag{41}$$

From the form of (41) we immediately deduce

Theorem 6. *For the ∞^1 curves of a "q" system which pass through a given point in a given direction, the geodesic curvature varies inversely as the square of the initial speed.*

Expanding (41) and using the identities (6) and (10), we get

$$\frac{1}{\rho^2} = \frac{1}{q^2 \dot{s}^4} \left[\sum_{kl} A_{kl} \phi_k \phi_l - \left(\sum_l \phi_l x'_l \right)^2 \right]. \tag{42}$$

Differentiating with respect to s and equating to zero gives

$$\dot{s}^3 \left[\sum_{kl} (A_{kl} \phi_k \phi_l)' - 2 \sum_l \phi_l x'_l \left(\sum_k (\phi_k x''_k + \sum_k \phi'_k x'_k) \right) \right]$$

$$- 4 \ddot{s} \left[\sum_{kl} A_{kl} \phi_k \phi_l - \left(\sum_l \phi_l x'_l \right)^2 \right] = 0,$$

[10] The euclidean analogues for dynamical trajectories in 3 and n dimensions of the results of this and the succeeding sections (except Theorem 6) were not considered in the articles mentioned in notes (1) and (2).

[11] Bianchi, ibid, p. 364.

where we have discarded the factor $1/\dot{s}^2$ whose vanishing leads to the geodesics, for which the hyperosculation property certainly holds.

By (9),

$$\ddot{s} = \sum_l \phi_l x'_l$$

and by (24),

$$x''_k = \frac{1}{q\dot{s}^2} \sum_l \phi_l (A_{kl} - x'_k x'_l) - \sum_{ij} \{ij,k\} x'_i x'_j \quad (k = 1, 2, \ldots n).$$

Substituting in above and solving for $\dot{s}^2$, we obtain

$$\dot{s}^2 = \frac{(4+\frac{2}{q}) \sum_l \phi_l x'_l \left[\sum_{ij} A_{ij} \phi_i \phi_j - (\sum_i \phi_i x'_i)^2 \right]}{\sum_{ijl} \frac{\partial}{\partial x_l} (A_{ij} \phi_i \phi_j) x'_l + 2 \sum_l \phi_l x'_l \left[\sum_{ijk} \phi_k \{ij,k\} x'_i x'_j - \sum_{ij} \frac{\partial \phi_i}{\partial x_j} x'_i x'_j \right]} \tag{43}$$

Thus, the necessary and sufficient conditions that the osculating geodesic circle at a point of a curve of a " q " system should there hyperosculate the curve, are that equations (38) and (43) should be satisfied.

Now, for a given direction x'_k $(k = 1, 2, \ldots, n)$, equation (43) determines one and only one value of $\dot{s}^2$, the square of the speed, so that, disregarding the geodesic, there is one and only one curve of a " q " system in each of the ∞^1 directions determined by equations (38), and hence there are only ∞^1 curves of the ∞^n curves which pass through a given point, which will there hyperosculate their corresponding geodesic circles. We may thus state

Theorem 7. *Of the ∞^n curves of a " q " system which pass through a given point, ∞^1 will there hyperosculate their corresponding geodesic circles, one curve in each of the ∞^1 initial directions generating the cone of Theorem* 4.

7. **Locus of Centers of Geodesic Curvature.** Consider the ∞^1 curves through a point M_0 which possess hyperosculating geodesic circles. The ∞^1 directions and the corresponding speeds must satisfy equations (38) and (43). In the flat tangent n-space S_n

to our curved n-space V_n at M_o, draw the tangent (straight) line in the direction of the principal geodesic normal ξ_k ($k=1, 2, \ldots, n$) of any one of these curves, and on this line lay off the corresponding radius of geodesic curvature ρ (measuring from M_o). The extremity P will be the center of geodesic curvature of the corresponding curve. What is the locus of all such points P for the ∞^1 curves of a "q" system through M_o which possess hyperosculating geodesic circles? We shall call this locus the *central locus*.

If, in V_n, we choose a system of geodesic parameters,[12] the element of length takes the form

$$ds^2 = dx_1^2 + \sum_{ij}^{2\ldots n} a_{ij}\, dx_i\, dx_j,$$

so that, throughout V_n,

$$a_{11} = A_{11} = 1, \quad a_{1j} = A_{1j} = 0 \quad (j \neq 1). \tag{44}$$

We may, in addition, choose the x_1 parameter curves, which are geodesics, so that the particular curve passing through M_o has the direction of the force vector $\sum_l A_{kl}\phi_l$ ($k=1, 2, \ldots, n$). We may, further, choose (without loss of generality) the other parameter curves so that they all form an orthogonal system at M_o. For this parameter system, we shall have, at M_o,

$$a_{ij} = A_{ij} = 0. \quad (i \neq j), \quad A_{ii} = \frac{1}{a_{ii}}. \tag{45}$$

$$\phi_k = 0. \quad (k = 2, 3, \ldots, n). \tag{46}$$

In S_n, let us take M_o as origin of coördinates and the tangent lines to the orthogonal parameter curves through M_o for the rectangular system of coördinate axes. If $y_k (k=1, 2, \ldots, n)$ are the rectangular coördinates of P and ω_k ($k=1, 2, \ldots, n$) are the angles between the principal geodesic normal and the coördinate axes, then

$$y_k = \rho \cos \omega_k = \rho\sqrt{a_{kk}}\,\xi_k = \rho^2\sqrt{a_{kk}}\,G_k \quad (k=1, 2, \ldots, n) \tag{47}$$

[12] Bianchi, ibid, pp. 336-337.

From (24) and (42)

$$G_1 = \frac{1}{q\dot{s}^2}\,\phi_1(1-x'_1{}^2),\ G_k = -\frac{1}{q\dot{s}^2}\,\phi_1 x'_1 x'_k\ (k=2,3,\ldots,n),$$

$$\frac{1}{\rho^2} = \frac{1}{q^2\dot{s}^4}\,\phi_1{}^2\,(1-x'_1{}^2);$$

hence,

$$y_1 = \frac{q\dot{s}}{\phi_1},\quad y_k = -\frac{\sqrt{a_{kk}}\,q\dot{s}^2 x'_1 x'_k}{\phi_1(1-x'_1{}^2)}\quad (k=2,3,\ldots,n) \tag{48}$$

Solving equations (48) for the x'_k in terms of the y_k, we get

$$\frac{y_k}{y_i} = \frac{\sqrt{a_{kk}}\,x'_k}{\sqrt{a_{ii}}\,x'_i};\quad \sum_k \sqrt{a_{kk}}\,y_k x'_k = 0;$$

hence,

$$\begin{cases} \dfrac{\sqrt{a_{kk}}\,x'_k}{x'_1} = -\dfrac{y_1 y_k}{y^2_2+y^2_3+\ldots+y^2_n}; \\ x'_1{}^2 = \dfrac{y^2_2+y^2_3+\ldots+y^2_n}{y^2_1+y^2_2+\ldots+y^2_n};\quad \dot{s}^2 = \dfrac{y_1\phi_1}{q} \end{cases} \tag{49}$$

Owing to our choice of parameter system at M_0, equations (38) and (43) reduce to

$$\begin{cases} \dfrac{\sum_\lambda \sqrt{A_{\lambda\lambda}}\,a_{2\lambda}x'_\lambda}{x'_2} = \dfrac{\sum_\lambda \sqrt{A_{\lambda\lambda}}\,a_{k\lambda}\,x'_\lambda}{x'_k}\ (k=3,4,\ldots,n) \\ a_{k\lambda} = \dfrac{\sqrt{a_{\lambda\lambda}}}{a_{kk}}\left[\tfrac{1}{2}\,\phi_1\,\dfrac{\partial a_{k\lambda}}{\partial x_1} + \dfrac{\partial \phi_k}{\partial x_\lambda}\right]\ (k=2,3,\ldots,n) \end{cases} \tag{50}$$

$$\dot{s}^2 = \frac{(2+\frac{1}{q})\,\phi^2_1 x'^2_1 (1-x'^2_1)}{\sum_\lambda \dfrac{\partial \phi_1}{\partial x_\lambda}\,x'_\lambda + x'_1 \sum_{\lambda\mu}\beta_{\lambda\mu}\,x'_\lambda x'_\mu};\quad \beta_{\lambda\mu} = -\tfrac{1}{2}\,\phi_1\,\frac{\partial a_{\lambda\mu}}{\partial x_1} - \frac{\partial \phi_\mu}{\partial x_\lambda}. \tag{51}$$

Substituting the values of x'_k from (49) into (50) and (51), these become

$$\sqrt{a_{22}}\, y_k \left\{ a_{21} \sum_{\lambda}^{2\ldots n} y^2{}_\lambda - y_1 \sum_{\lambda}^{2\ldots n} a_{2\lambda}\, y_\lambda \right\}$$

$$= \sqrt{a_{kk}}\, y_1 \left\{ a_{k1} \sum_{\lambda}^{2\ldots n} y^2{}_\lambda - y_1 \sum_{\lambda}^{2\ldots n} a_{k\lambda}\, y_\lambda \right\} \quad (k=3, 4, \ldots . n), \tag{52}$$

$$\frac{\partial \phi_1}{\partial x_1} y_1 \sum_{\lambda}^{2\ldots n} y^2{}_\lambda - \sum_{\lambda}^{1\ldots n} y_\lambda{}^2 \sum_{\lambda}^{2\ldots n} \frac{1}{\sqrt{a_{\lambda\lambda}}} \frac{\partial \phi_1}{\partial x_\lambda}\, y_\lambda$$

$$+ \sum_{\lambda}^{2\ldots n} y^2{}_\lambda \sum_{\lambda}^{2\ldots n} \frac{1}{\sqrt{a_{\lambda\lambda}}} \left(\frac{\partial \phi_1}{\partial x_\lambda} + \frac{\partial \phi_\lambda}{\partial x_1} \right) y_\lambda$$

$$+ y_1 \sum_{\lambda\mu}^{2\ldots n} \frac{\beta_{\lambda\mu}}{\sqrt{a_{\lambda\lambda}}\sqrt{a_{\mu\mu}}}\, y_\lambda\, y_\mu = (2q+1)\, \phi_1 \sum_{\lambda}^{2\ldots n} y^2{}_\lambda . \tag{53}$$

The $(n-2)$ equations (52), being homogeneous equations of the third degree in the coördinates, are the equations of $(n-2)$ cubic hypercones (spreads of $(n-1)$ dimensions) or the equations of a cone (spread of two dimensions) of order 3^{n-2} common to the $(n-2)$ hypercones. This cone has for generators the lines drawn through M_o in the directions of the principal geodesic normals to the curves. A study of equations (52) shows that any plane through the axis $M_o y_1$ cuts each of the hypercones twice in $M_o y_1$, so that the axis $M_o y_1$, or the force vector, is a double generator of each of the $(n-2)$ hypercones. Hence, we have

Theorem 8. *The lines drawn in the directions of the principal geodesic normals to the ∞^2 curves through a given point which there hyperosculate their corresponding osculating geodesic surfaces, generate a cone of order 3^{n-2}, the same for all "q" systems in a given field of force. This cone contains the force vector as a generator.*

Equation (53), being of the third degree in the coördinates and containing no terms of lower degree than the second, is the equation of a cubic hypersurface with a double point at M_o, so that any straight line through M_o cuts it in only one other point. This hypermoniod also contains the axis $M_o y_1$, or the force vector as a generator.

Equations (52) and (53) define, in general, a curve of order 3^{n-1}, *viz.*, the curve of intersection of the $(n-2)$ cubic hypercones and the cubic hypermonoid. But the order of the required locus is actually much lower than 3^{n-1}, since the $(n-1)$ hypersurfaces have in common the force vector and also the quadratic conical spread of $(n-2)$ dimensions

$$y_1 = 0\,, \quad \sum_{\lambda}^{2\ldots n} y_\lambda{}^2 = 0, \tag{54}$$

composed of the minimal straight lines through M_0 and lying in the hyperplane perpendicular to the force vector. The required central locus is the residual curve of intersection.

Theorem 9. *The locus of centers of geodesic curvature of the* ∞^1 *curves of a "* q *" system through a point* M_0 *which possess hyperosculating geodesic circles, is, in general, a curve of order* 3^{n-1}, *the intersection of* $(n-2)$ *cubic hypercones with vertices at* M_0 *and a cubic hypermonoid with* M_0 *as double point. These spreads contain the force vector through* M_0 *and also the quadratic conical spread of* $(n-2)$ *dimensions composed of the minimal straight lines of the hyperplane perpendicular to the force vector at* M_0.

8. **The Central Locus in Spaces of 2, 3, and 4 Dimensions.** As stated in § 7, the $(n-1)$ cubic hyperspreads (52) and (53) have in common the central locus as well as the force vector and a quadratic spread of $(n-2)$ dimensions. The order of the central locus must therefore be less than 3^{n-1}. We shall now determine the order of the central locus for "q" systems in spaces of 2, 3 and 4 dimensions.

"q" *systems in* V_2. In a space of two dimensions or ordinary surface, the osculating geodesic surface at a point M_0 of a curve on the surface coincides with the surface, so that equations (52) reduce to the equation of the tangent plane at M_0, and equation (53) reduces to the straight line $y_2 = 0$ (the force vector) and the conic

$$\sqrt{a_{22}}\,\frac{\partial \phi_1}{\partial x_2}\,y_1^2 - \sqrt{a_{22}}\,\frac{\partial \phi_2}{\partial x_1}\,y_2^2 + \left(\tfrac{1}{2}\,\phi_1\,\frac{\partial a_{22}}{\partial x_1} - a_{22}\,\frac{\partial \phi_1}{\partial x_1} + \frac{\partial \phi_2}{\partial x_2}\right) y_1\,y_2 + (2q+1)\,a_{22}\,\phi_1\,y_2 = 0, \tag{55}$$

passing through M_0 in the direction of the force vector. This conic becomes a rectangular hyperbola when and only when the sum of the coefficients of y_1^2 and y_2^2 is zero, *ie.*, when and only when

$$\frac{\partial \phi_1}{\partial x_2} = \frac{\partial \phi_2}{\partial x_1};$$

but this is the condition that the force should be conservative. Hence, we have

Theorem 10. *For a "q" system on a surface, the locus of centers of geodesic curvature of the ∞^1 curves through a given point which there hyperosculate their corresponding geodesic circles, is a conic passing through the point in the direction of the force vector. This conic is a rectangular hyperbola when and only when the field of force is conservative.*[12]

"q" systems in V_3. In a space of three dimensions, equations (52) become the equation of the cubic cone.

$$(y^2_2 + y^2_3)\left(y_3 \frac{\partial \phi_2}{\partial x_1} - y_2 \frac{\partial \phi_3}{\partial x_1}\right) = y_1\left[\sqrt{a_{22}}\, y_3 (a_{22} y_2 + a_{23} y_3) - \sqrt{a_{33}}\, y_3 (a_{32} y_2 + a_{33} y_3)\right]. \tag{56}$$

We may thus combine Theorems 4, 5, and 8 into

Theorem 11. *For the ∞^2 curves of a "q" system through a given point in any space of three dimensions which are hyperosculated by their corresponding osculating geodesic surfaces, the ∞^1 initial directions generate a quadratic cone and the ∞^1 directions of their principal geodesic normals generate a cubic cone. Each of these cones contains the force vector as a generator.*

Equation (53) becomes the equation of the cubic monoid

$$(y^2_2+y^2_3)\left(\frac{1}{\sqrt{a_{22}}}\frac{\partial \phi_2}{\partial x_1} y_2 + \frac{1}{\sqrt{a_{33}}}\frac{\partial \phi_3}{\partial x_1} y_3 + \frac{\partial \phi_1}{\partial x_1} y_1\right) - y^2_1\left(\frac{1}{\sqrt{a_{22}}}\frac{\partial \phi_1}{\partial x_2} y_2 + \frac{1}{\sqrt{a_{33}}}\frac{\partial \phi_1}{\partial x_3} y_3\right) + y_1\left[\frac{1}{a_{22}}\gamma_{22} y^2_2 + \frac{1}{\sqrt{a_{22}}\sqrt{a_{33}}}(\gamma_{23}+\gamma_{32}) y_2 y_3 + \frac{1}{a_{33}}\gamma_{33} y^2_3\right] = (2q+1)\,\phi_1 (y^2_2+y^2_3). \tag{57}$$

[12] This theorem was obtained by the author in the paper mentioned in note (3).

In general, the cubic surfaces intersect in a curve of the ninth order. But these surfaces have in common the axis $M_o y_1$ or force vector, which is a double line on the cone and a single line on the monoid, and also the two minimal lines $y_1=0$, $y^2_2+y^2_3=0$. These four right lines through M_o evidently reduce the equation of the residual curve of intersection to one of the fifth order. Hence,

Theorem 12. *For a "q" system in any space of three dimensions, the locus of the centers of geodesic curvature of the curves through a given point which have hyperosculating geodesic circles, is a quintic curve.*

"q" systems in V_4. In a space of four dimensions, equations (52) become the equations of two cubic hypercones.

$$\begin{cases} \left(y_3\dfrac{\partial\phi_2}{\partial x_1}-y_2\dfrac{\partial\phi_3}{\partial x_1}\right)\sum\limits_{\lambda}^{2\ldots4} y^2_\lambda = y_1\left[\sqrt{a_{22}}\,y_2\sum\limits_{\lambda}^{2\ldots4} a_{2\lambda}y_\lambda-\sqrt{a_{33}}\,y_2\sum\limits_{\lambda}^{2\ldots4} a_{2\lambda}\,y_\lambda\right], \\ \left(y_4\dfrac{\partial\phi_2}{\partial x_1}-y_2\dfrac{\partial\phi_4}{\partial x_1}\right)\sum\limits_{\lambda}^{2\ldots4} y^2_\lambda = y_1\left[\sqrt{a_{22}}\,y_4\sum\limits_{\lambda}^{2\ldots4} a_{2\lambda}\,y_\lambda-\sqrt{a_{44}}y_2\sum\limits_{\lambda}^{2\ldots4} a_{4\lambda}\,y_\lambda\right]. \end{cases} \tag{58}$$

Equation (53) becomes the equation of the hypermonoid

$$\sum_{\lambda}^{2\ldots4} y_\lambda{}^2\cdot\sum_{\lambda}^{1\ldots4}\frac{1}{\sqrt{a_{\lambda\lambda}}}\frac{\partial\phi_\lambda}{\partial x_1}y_\lambda-y^2_1\sum_{\lambda}^{2\ldots4}\frac{1}{\sqrt{a_{\lambda\lambda}}}\frac{\partial\phi_1}{\partial x_\lambda}y_\lambda+y_1\sum_{\lambda\mu}^{2\ldots4}\frac{\gamma_{\lambda\mu}}{\sqrt{a_{\lambda\lambda}}\sqrt{a_{\mu\mu}}}y_\lambda y_\mu$$
$$=(2q+1)\,\phi_1\sum_{\lambda}^{2\ldots4} y_\lambda{}^2. \tag{59}$$

In general, these cubic hypersurfaces intersect in a curve of the twenty-seventh order. But these hypersurfaces have in common the axis $M_o y_1$ or force vector, which is a double line on each of the cubic hypercones and a single line on the cubic hypermonoid, and also the quadratic minimal cone $y_1=0$, $y^2_2+y^2_3+y^2_4=0$. In order to find the order of the residual curve of intersection, let us cut the hypersurfaces by an arbitrary hyperplane S_3. This hyperplane will, in general, have 27 points in common with the three hypersurfaces, which are the points of intersection of S_3 and the curve of order 27. Now S_3 will cut each of the hypersurfaces in a cubic surface, and these three cubic surfaces have, in general, the above 27 points in common. But S_3 also cuts

the common generator M_0y_1 in a point P, which is a double point on two of the cubic surfaces, and cuts the common quadratic minimal cone in a conic, which lies on all three cubic surfaces. We have thus reduced our four dimensional problem to a three dimensional one. In S_3 we have three cubic surfaces with a conic in common; they also contain a point P which is a double point on two of these surfaces and which does not lie on the conic. What is the residual number of points of intersection of these surfaces? The conic will reduce the number by 12.[13] The point P will evidently reduce the number by 4. The three cubic surfaces thus have 11 residual points in common, or S_3 cuts the residual curve of intersection of the three hypersurfaces in 11 points. Since S_3 is an arbitrary hyperplane, the residual curve of intersection must be of the eleventh order. Hence, we have

Theorem 13. *For a "q" system in any space of four dimensions, the locus of centers of geodesic curvature of the curves through a given point which have hyperosculating geodesic circles, is a curve of the eleventh order.*

[13]See *A Treatise on the Analytic Geometry of 3 Dimensions*, by George Salmon, revised by R. A. P. Rogers, fifth edition, Vol. 1, p. 370. If three surfaces of degrees μ, ν, ρ, have a curve of degree m in common, this curve absorbs $m(\mu+\nu+\rho-2)-r$ points of intersection, where r is the number of tangents to the common curve which intersect an arbitrary straight line in space. In our problem, we evidently have $\mu=\nu=\rho=3, m=2, r=2$.

THE EQUATION OF STATE, WITH APPLICATIONS TO VISCOSITY

By H. B. PHILLIPS

1. For some years Prof. F. G. Keyes[1] has used an equation of state of the form

$$p = \frac{R\,T}{V - \beta e^{\frac{\alpha}{V}}} - \frac{A}{(V-l)^2}, \qquad (1)$$

where p, V, T are pressure, volume, temperature, R is the gas constant, and α, β, A, l are constants characteristic of the substance. This equation has been found to represent the pressure of a number of gases within the error of measurement provided the values of V, T are not too near the saturation curve, and also to represent the pressure of liquids fairly well. It is expected to apply to fluids containing a single type of molecule over ranges of volume and temperature within which no changes of polymerisation or association occur. In this paper I give a general discussion of this type of equation and apply it to the calculation of viscosities.

2. **A general type of system.** The equation of Keyes, like that of van der Waals, belongs to the general type

$$p = T\psi(V) - \phi(V), \qquad (2)$$

in which the pressure is a linear function of the temperature with coefficients that are functions of the volume. Substances for which this is true have other simple properties that entitle them to special consideration.

If S is the entropy and U the energy, (2) combined with the general thermodynamic equation

$$dU = T\,dS - p\,dV \qquad (3)$$

gives

$$dU = T[dS - \psi(V)\,dV] - \phi(V)\,dV. \qquad (4)$$

[1] A New Equation of Continuity, Proc. Nat. Acad. Science, 3(323-330).

Since dU and $\phi(V)dV$ are both exact differentials,

$$T[dS - \psi(V)dV]$$

must be exact. Hence

$$dS - \psi(V)dV$$

is the differential of a function of the temperature, and so

$$S = \int \psi(V)dV + F(T) = \chi(V) + F(T) \tag{5}$$

is the sum of a function of the temperature and a function of the volume. Conversely, if the entropy has this form, substitution in (3) gives

$$dU = TF'(T)dT + [T\psi(V) - p]dV \tag{6}$$

Since the first two terms of this expression are exact differentials

$$T\psi(V) - p$$

must be a function of the volume and so p has the form (2).

Equations (2) and (6) give

$$U = \int TF'(T)dT + \int \phi(V)dV = K(T) + P(V) \tag{7}$$

showing that the energy is the sum of a function of the temperature and a function of the volume. Conversely, if the energy has this form, from (3) we have

$$dS = F'(T)\,dT + \frac{1}{T}[p + \phi(V)]dV,$$

whence

$$\frac{1}{T}[p + \phi(V)]$$

is a function of the volume and so the pressure is given by an equation of the form (2).

From (7) the specific heat at constant volume is

$$C_v = \frac{\partial U}{\partial T} = K'(T) \tag{8}$$

which is a function of the temperature only. Conversely, from (8) we find that the energy has the form (7) and so the pressure has the form (2).

From any one of the equations (2), (5), (7) (8) each of the others can then be obtained. If a substance has any one of these prop-

erties it has all the others. That the pressure is a linear function of the temperature in case there is no change of association is indicated by such approximations as Charles' law and van der Waals' equation and by the experimental work of Amagat,[2] Ramsey and Young.[3] Keyes, and others. If the temperature is proportional to the average kinetic energy per degree of freedom, in case of invariable molecules the distribution in velocity will depend on the temperature only and that in configuration on the volume only, the probability of a given distribution will be the product of a function of the temperature and a function of the volume, and so the entropy

$$S = K \log W$$

will be the sum of such functions as indicated by (5). If the energy can be considered as the sum of two parts, the one kinetic due to the motion of the molecules, the other potential due to their relative positions, the first from kinetic theory (even in case of quantum theory) is a function of the temperature and the second a function of the volume. Hence the energy has the form (7). The specific heat at constant volume is very difficult to measure. The variation with volume that has been obtained is very small and that may be accounted for by changes of molecular association. It seems therefore reasonable to assume that the properties (2), (5), (7), (8) are satisfied by a substance in such changes of state as do not involve a change in the character of its molecules.

3. **The Gibbs surface.** The state of a system consisting of one component is determined by two variables. Three variables are then connected by an equation. Gibbs showed that the equation

$$U = f(S, V) \tag{9}$$

connecting energy, entropy, and volume is a fundamental equation,[4] in the sense that from it by differentiation and algebraic processes all the thermodynamic variables can be obtained.

[2] Ann. chim. phys., 29 (505).
[3] Zeit. fur phys. Chem. 1 (440).
[4] Scientific Papers, I (86).

Taking U, S, V as the coördinates of a point in three dimensions, equation (9) represents a surface called the Gibbs surface.

In the case just discussed this surface has a particularly simple form. The equations

$$\left.\begin{array}{l} U=K(T)+P(V) \\ S=F(T)+\chi(V) \end{array}\right\} \tag{10}$$

show that if T is kept constant, the curve obtained by varying V has the same form whatever constant value of T is used. The isothermals on the Gibbs surface are therefore all alike. Any one can be moved into any other by a displacement parallel to the US-plane. Similarly the constant volume lines are all alike. The surface, called a translation surface, can be generated by the motion (without rotation) of an isothermal or an isochore.

If then we determine the values of the energy and entropy along one isothermal and one isochore, we can construct the surface by moving the isothermal along the isochore and so determine the thermodynamic properties of the substance at all other volumes and temperatures for which the equations (10) are valid.

4. **The kinetic pressure.** To obtain the functions $\psi(V)$ and $\phi(V)$ in equation (2) it is necessary to have some hypothesis as to their origin. We assume that

$$T\psi(V)$$

is the kinetic pressure due to the bombardment of the molecules at a point within the fluid. The external pressure p is less than this by the cohesive pressure $\phi(v)$ due to the mutual potential energy of the molecules.

Let m be the mass of a molecule, u its x-component of velocity, ν the number of molecules per unit volume, and

$$\nu f(u)\,du$$

the number of these with components of velocity between u and $u+du$. If the molecules did not interfere with each other, the number of these that would cross unit area of the xy-plane in unit time would be

$$\nu u f(u)\,du$$

and the x-component of momentum transferred would be

$$\vartheta\, m\, u^2 f(u)\, du$$

This is equivalent to a pressure over this area equal to

$$\int_{-\infty}^{\infty} \vartheta\, m\, u^2 f(u)\, du = \vartheta\, av.\, (m\, u^2) = \rho\, RT, \qquad (11)$$

where ρ is the density.

Equation (11) gives the pressure of a perfect gas. It is obtained on the assumption that each molecule describes its path uninfluenced by the others. Any interaction of the molecules will increase this pressure, for the distribution of velocities is assumed to be the same in any case. Interaction of the molecules will increase their migration and so increase the transfer of momentum, or pressure.

Consider a thin section of the fluid between parallel planes perpendicular to the x-axis. By observing the molecules cross unit area of one of these planes we obtain a rate of transfer of momentum I equal to the pressure. By observing the molecules between the two planes at a particular instant, and dividing them into two currents in opposite directions, we obtain the total rate of transfer (11). The two results are not the same. For the brief time dt we must observe the molecules to obtain I must be long enough for a large number of molecules to cross so that we may have an average result. Even in this brief time a fraction $RIdt$ of the total transfer Idt will be reflected back. This reflection will occur across the boundary equally in both directions and so will not affect the distribution between the planes but will be counted twice by the observer at a particular boundary. Therefore the difference

$$I - RI = \rho\, RT \qquad (12)$$

will be the rate of transfer observed between the planes at a particular instant of time.

Since the molecules themselves are the elementary reflectors, if the density is very small so that they may be supposed to act independently, the percentage of I reflected will be proportional to the density and so

$$R = b\rho \qquad (13)$$

where b is constant. From (12) the kinetic pressure is then

$$I = \frac{\rho RT}{1 - b\rho} = \frac{RT}{V - b} \tag{14}$$

as given by van der Waals' equation. In this the quantity b has the dimensions of a volume but is not here regarded as connected in any way with the volume of the molecules. In fact, if the molecules influence each other, the quantity b will exist even if the volume occupied by the molecules is indefinitely small.

The co-volume b is a measure of the reflecting power per molecule. At higher densities this action of a molecule may be interfered with by other molecules. If this effect is additive, we will have

$$d\,b = -\alpha\, b\, d\,\rho$$

where α is constant, as the change produced by an increase $d\,\rho$ in the density. Integration of this gives

$$b = \beta e^{-\alpha\rho} = \beta e^{-\frac{a}{v}} \tag{15}$$

as in the equation of Keyes.

5. **The cohesive pressure.** The mutual potential energy of two molecules is a function of their distance and relative orientation. In an infinite mass of a fluid the number of molecules at each distance from a given one and having with respect to it a given orientation is proportional to the density. The same is true of a given number of molecules. The potential energy of a gram of the fluid is then

$$P = A\,\rho = \frac{A}{V} \tag{16}$$

where A is constant. This is true whatever be the law of force between the molecules, provided merely that the law is independent of the density and that the force diminish at great distances sufficiently for the integrals with infinite limits to converge. Since atoms of electronic model are polarized, it may be that two atoms attract when oriented in certain ways and repel when

oriented in others. Equation (16) is still valid if the distribution of orientations is independent of the density.

If the force between molecules is appreciable only at very short distances, equation (16) is valid for a mass of fluid in a finite domain, for the molecules within the fluid have the same potential energy as before and the number near the surface is not great enough appreciably to affect the result. That such is the case is evident since the pressure depends only on the volume and not on the shape of the containing vessel. The cohesive pressure is then

$$\phi = -\frac{\partial P}{\partial V} = \frac{A}{V^2} \tag{17}$$

as given by van der Waals.

Now a study of pressure data shows that the cohesive pressure of gases is represented better by an expression of the form

$$\phi = \frac{A}{(V+l)^2} \tag{18}$$

than by (17). This indicates that the force between two molecules is not determined simply by their mutual positions but changes with the density. One way of explaining this is by the variation in the dielectric constant. In a dielectric of inductivity k, the force between given charges is equal to the force that would exist if the dielectric were air divided by k. If then the molecules can be treated as substantially invariable electrical systems, all the forces which determine the cohesive pressure are reduced in this same ratio and so (17) must be replaced by

$$\phi = \frac{A}{kV^2}. \tag{18}$$

According to the theory of Lorentz,[8] in case of a gas

$$\frac{k-1}{k+2} = C\rho$$

where C is constant. Solving this for k and substituting in (18) we get

$$\phi = \frac{A(V-C)}{V^2(V+2C)} = \frac{A}{V^2}\left(1 - \frac{3C}{V} \ldots\right). \tag{19}$$

[8] Richardson, Electron Theory of Matter, p. 73.

Since the ratio of C to V is usually very small, within the precision of the data, this is equal to

$$\frac{A}{(V+l)^2} = \frac{A}{V^2}\left(1-\frac{2l}{V}\cdots\right)$$

if we take

$$l = {}^3/_2\, C.$$

From pressure measurements it is very difficult to determine the quantity l. It is determined graphically as the intercept on a coördinate axis of the line obtained by using V and

$$\frac{1}{\sqrt{\phi}}$$

as coördinates. A small error of slope may change its value greatly. In some cases it even has the wrong algebraic sign. Recent work on methane gives

$$l = .566$$

with a precision of perhaps a few per cent. Using the value

$$k = 1.00095$$

at 0°C. and 1 atmosphere, we get

$$C = .41 \qquad {}^3/_2\, C = .61$$

which agrees with the measured value of l as well as could be expected.

6. **The viscosity of a gas.** Let u_0 be the x-component of the velocity of the gas (mass motion) at the point (x, y, z). Let the gas flow parallel to the x-axis in such a way that

$$\frac{\partial u_0}{\partial z} = 1 \tag{21}$$

Under these conditions the viscosity η of the gas is defined as the total momentum transferred across unit area of the xy-plane in unit time. To find the viscosity we therefore find the number of molecules with each velocity crossing unit area and multiplying in each case by the average x-momentum.

Let ν be the number of molecules per cubic centimeter and w the z-component of the velocity of a molecule. As in §4, if the

molecules did not interfere with each other, the number with velocity components between w and $w+dw$ that would cross unit area of the xy-plane in unit time would be

$$\nu w f(w)\, dw$$

But because of interference the number that do cross is

$$\frac{\nu w}{1-b\rho} f(w) dw = \frac{\rho}{1-b\rho}\,\frac{w}{m} f(w)\, dw\,. \tag{22}$$

Tracing the motion of a given molecule from the xy-plane backward in its course, the distance from that plane at which it probably had a given interaction with other molecules is inversely proportional to the density. The average momentum acquired in any such interaction is proportional to the reflection coefficient b. Therefore in a field of unit velocity gradient (21) the average momentum parallel to the x-axis carried by a molecule of velocity component w has the form

$$\frac{b}{\rho} F(w)\,.$$

Combining (22) and (23) we obtain for the total transfer of x-momentum across unit area the expression

$$\eta = \frac{b}{1-b\rho}\int_0^\infty \frac{w}{m} f(w) F(w)\, dw = \frac{bK}{1-b\rho} \tag{24}$$

where K is a function of the temperature only.

In the following table are given measured viscosities together with the calculated values of

$$K = \eta\,\frac{(1-b\rho)}{b}\,.$$

From Amagat's pressure measurements Keyes[6] finds for carbon dioxide

$$\log b = .4650 - \frac{.7065}{V} \tag{25}$$

Inspection of the table shows that at each temperature the variations in K show no particular trend for densities less than about 0.2. At densities greater than this (25) ceases to hold satisfactorily.

[6] J. Am. Soc. Ref. Eng. 3 (7).

Viscosity of Carbon Dioxide[7] — Gas Phase

T	p	ρ	$\log b$	$\eta \times 10^6$	$K \times 10^5$
20°	1	.00183	.4637	148	5.07
	20	.036	.4383	156	5.12
	40	.100	.3944	166	5.03
	50	.145	.3626	177	5.11
	56	.190	.3308	186	5.15
30°	1	.00177	.4637	153	5.23
	20	.0354	.4400	159	5.21
	40	.092	.4000	168	5.14
	60	.177	.3400	187	5.24
	70	.287	.2622	299	5.95
32°	1	.00176	.4638	155	5.30
	20	.0352	.4401	162	5.31
	40	.090	.4014	175	5.36
	60	.170	.3449	187	5.27
	70	.255	.2848	214	5.65
	74	.360	.3107	254	6.49
35°	1	.00174	.4638	156	5.33
	20	.0348	.4404	163	5.35
	40	.085	.4015	174	5.42
	60	.163	.3498	178	5.05
	70	.227	.3046	214	5.75
	75	.289	.2608	237	6.15
40°	1	.00173	.4638	157	5.37
	23.8	.0408	.4362	169	5.50
	40	.083	.4064	176	5.34
	60	.153	.3569	187	5.43
	70	.204	.3209	200	5.47
	80	.291	.2594	218	5.65

[7] Phillips, Proc. R. Soc. 87 (46).

7. **Vicosity of liquids.** In the case of a liquid I assume that the molecules vibrate about positions of equilibrium as in a solid. Due to the mass motion of the fluid these equilibrium positions change with the time, but similar changes occur at neighboring points so that the structure of the liquid near a given molecule varies slowly in comparison with the motion of the molecule. This motion is therefore substantially periodic and so may be expected to obey the laws of quantum theory.

We may consider the motion of a molecule in two ways both leading to the same formula for viscosity. First we may assume the time of interaction of two molecules as very brief followed by a much longer period of practically uniform motion and that the velocity relative to the fluid is acquired during the brief interaction. Suppose then a molecule reaching the xy-plane has been moving for a time t since the last collision. From (21) its momentum parallel to the x-axis will on the average be

$$mwt,$$

where w is the velocity perpendicular to the xy-plane. Since w is constant over practically the entire period

$$m\,w\,t = \frac{1}{w}\int_0^t m\,w^2\,dt\ .$$

The molecule in the time t will on the average describe a complete mean free path, that is, a half period in the sense of quantum theory. According to Sommerfeld's theory we therefore have

$$2\int_0^t m\,w^2\,dt = n\,h\ , \tag{26}$$

where n is an integer. Consequently the average x-momentum transferred is

$$m\,w\,t = \frac{n\,h}{2w} \tag{27}$$

From (22) the viscosity is then

$$\eta = \frac{nh\,\rho}{2m(1-b\rho)}\int_{-\infty}^{\infty} f(w)dw = \frac{nh\,\rho}{2m(1-b\rho)} = \frac{n\,Nh}{2M(V-b)}\ , \tag{28}$$

where N is the number of molecules per mol and M the molecular weight of the substance.

A second method is to consider the action as extending along the whole path of the molecule. At the distance z from the xy-plane the average velocity is equal to the mass motion of the fluid which by (21) may be taken as z. The molecule in moving through the fluid may be considered as subject to a sort of drag proportional on the average to the velocity of the fluid. Molecules reaching the xy-plane with velocity w may then be considered as deriving this velocity at the average distance

$$\bar{z} = \frac{\int z\,dw}{\int dw} = \frac{z\,w\,\Big|_{w=0}^{z=0} - \int w\,d\,z}{\int dw} = \frac{\int w^2\,dt}{w}$$

and so have an average momentum equal to

$$m\bar{z} = \frac{\int m\,w^2\,dt}{w} = \frac{n\,h}{2w}$$

as in (27). The viscosity is then given by (28) as before.

A comparison of (28) with experiment is given in an article now being published in the Proceedings of the National Academy of Sciences. In all cases it turns out that $n=6$ so that (28) takes the form

$$\eta\,(V-b) = \frac{3N}{M}\,h\,. \qquad (29)$$

It is to be noted that $3N/M$ is the number of translational degrees of freedom in the volume V of the liquid. This suggests that the equation might be derived by a more general procedure using the gram of fluid as the elementary mechanical system.

SOME HYDRODYNAMIC ASPECTS OF GROUP THEORY

By S. D. ZELDIN

In a paper published in 1900[1] E. J. Wilczynski has shown the possible types of projective and linearoid groups for fluid in steady motion. In the present paper I shall discuss some of the invariant configurations of the motion subject to those groups.

1. We shall begin by reviewing briefly the principal results obtained by Wilczynski. Let x, y, z be the Cartesian coördinates of any point of the fluid at the time t. Considering t as a parameter, the general infinitesimal transformation of a one-parameter group is

$$Kf = u(x, y, z)\frac{\partial f}{\partial x} + v(x, y, z)\frac{\partial f}{\partial y} + w(x, y, z)\frac{\partial f}{\partial z} \tag{1}$$

The finite equations of the group can be found by integrating the differential equations.

$$\frac{dx}{dt} = u, \quad \frac{dy}{dt} = v, \quad \frac{dz}{dt} = w. \tag{2}$$

Thus u, v, w represent the velocity-components at the point x, y, z.

If X, Y, Z denote the components of the force acting upon the unit of mass, p the pressure, and ρ the density at the point x, y, z, then Euler's equations take the form:

$$\begin{aligned} Ku &= X - \frac{1}{\rho}\frac{\partial p}{\partial x}, \\ Kv &= Y - \frac{1}{\rho}\frac{\partial p}{\partial y}, \\ Kw &= Z - \frac{1}{\rho}\frac{\partial p}{\partial z}, \end{aligned} \tag{3}$$

[1] Trans. Am. Math. Soc., V. 1, pp. 339–352.

and the equation of continuity becomes:

$$K\rho+\rho\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}\right)=0. \tag{4}$$

If the forces X, Y, Z have a potential so that

$$X=\frac{\partial V}{\partial x}, Y=\frac{\partial V}{\partial y}, Z=\frac{\partial V}{\partial z}. \tag{5}$$

then the functions u, v, w must satisfy the equations

$$\frac{\partial Kv}{\partial z}-\frac{\partial Kw}{\partial y}=0, \frac{\partial Kw}{\partial x}-\frac{\partial Ku}{\partial z}=0, \frac{\partial Ku}{\partial y}-\frac{\partial Kv}{\partial x}=0. \tag{6}$$

Because of those conditions it has been proved by Wilczynski that *an arbitrary projective one-parameter group cannot represent the steady motion of a fluid under the influence of forces possessing a potential. To represent such a motion, the group must be a linear group.* If

$$Kf=u\frac{\partial f}{\partial x}+v\frac{\partial f}{\partial y}+w\frac{\partial f}{\partial z}, \tag{7}$$

where

$$\begin{aligned} u&=\gamma_1+c_{11}x+c_{21}y+c_{31}z, \\ v&=\gamma_2+c_{12}x+c_{22}y+c_{32}z, \\ w&=\gamma_3+c_{13}x+c_{23}y+c_{33}z, \end{aligned} \tag{8}$$

is the infinitesimal transformation of this linear group, the coefficients c_{kl} must satisfy the three conditions:

$$\left\{\begin{aligned} &\sum_{k=1}^{3}\left(c_{k3}\,c_{2k}-c_{k2}\,c_{3k}\right)=0, \\ &\sum_{k=1}^{3}\left(c_{k1}\,c_{3k}-c_{k3}\,c_{1k}\right)=0, \\ &\sum_{k=1}^{3}\left(c_{k2}\,c_{1k}-c_{k1}\,c_{2k}\right)=0, \end{aligned}\right. \tag{9}$$

which necessary conditions are also sufficient.

2. To determine the configurations which remain invariant during the motion of the fluid, it is necessary to find the functions

or equations which admit the infinitesimal transformation Kf, *i.e.*, for f to be invariant we must have

$$Kf=0. \tag{10}$$

Now it is clear that the solutions of the equations

$$\frac{dx}{dt} = u(x, y, z), \frac{dy}{dt} = v(x, y, z), \frac{dz}{dt} = w(x, y, z)$$

are invariants of the group. So that, if

$$u_1(x, y, z) = \text{constant}, u_2(x, y, z) = \text{constant}$$

are solutions of those equations, they represent two families of surfaces invariant under the group, *i.e.*,

$$Ku_1=0, \quad Ku_2=0$$

Moreover, the intersections of these surfaces are the lines of flow of the fluid. It is interesting to find out whether there exist separate invariant points, or other geometrical configurations in addition to those lines of flow.

Now, it has been shown by Lie[2] that the points whose coördinates satisfy the equations

$$u(x, y, z)=0, v(x, y, z)=0, \ w(x, y, z)=0 \tag{11}$$

are separately invariant. It may happen of course that equations (11) are not only satisfied by a discrete number of points, but by all points of a curve or several curves; furthermore, equations (11) may even be satisfied by all points of a surface or several surfaces.

Let us therefore consider the fluid motion expressed by the ternary linear group. In equations (8) we can put $\gamma_i=0$, since the motions for which $\gamma_i \neq 0$ differs from those for which $\gamma_i=0$ by a translation. We also assume that the origin remains fixed during the entire motion. The infinitesimal transformation of this group will be

[2] Lie-Scheffers, Differentialgleichungen, p. 241.

$$
\begin{aligned}
&(c_{11}x+c_{21}y+c_{31}z)\frac{\partial f}{\partial x}\\
&+(c_{12}x+c_{22}y+c_{32}z)\frac{\partial f}{\partial y}\\
&+(c_{13}x+c_{23}y+c_{33}z)\frac{\partial f}{\partial z}.
\end{aligned}
\tag{12}
$$

By considering the components of the velocity of rotation of any element of the fluid it has been shown[3] by Wilczynski that by choosing the coördinates properly we shall have

$$c_{23}=c_{32},\quad c_{31}=c_{13},\quad c_{12}=c_{21}+2\omega \tag{13}$$

where ω is the angular velocity of rotation and equals $\frac{1}{2}(c_{11}-c_{21})$. And since the forces have a potential, we have from equations (9) the following:

$$(c_{11}+c_{22})\omega=0,\quad c_{23}\omega=0,\quad c_{31}\omega=0. \tag{14}$$

Therefore either $\omega=0$, or

$$c_{11}+c_{22}=0,\quad c_{23}=0,\quad c_{31}=0. \tag{15}$$

If $\omega=0$, the coefficients of the partial derivatives in equations (12) being equated to zero give by the aid of (13) and (14)

$$
\begin{aligned}
c_{11}x+c_{21}y+c_{31}z&=0,\\
c_{21}x+c_{22}y+c_{32}z&=0,\\
c_{31}x+c_{32}y+c_{33}z&=0.
\end{aligned}
\tag{16}
$$

It is evident that the point $x=y=z=0$ satisfies those equations and is therefore invariant, which is also true by assumption. In order that equations (16) should have other than zero solutions, *the determinant of the coefficients, which will be denoted by* Δ_1, *should vanish.*

If the rank of Δ_1 is two equations (16) have one non-zero solution. Suppose that the point (x_1, y_1, z_1) satisfies those equations, then the points (mx_1, my_1, mz_1) will also satisfy (m is an arbitrary constant). With respect to the steady motion it

[3] Tran. Am. Math. Soc., p. 345.

means that *there will be a straight line passing through the origin which remains invariant during the entire motion*, moreover *every point on that line is invariant.*

If the rank of Δ_1 is one there will be *an invariant plane passing through the origin, every point of which remains invariant during the entire motion.*

In the case when $\omega \neq 0$ the determinant of the coefficients in equations (16) takes the form

$$\Delta_2 \equiv \begin{vmatrix} c_{11} & c_{21} & 0 \\ c_{12} & -c_{11} & 0 \\ 0 & 0 & c_{33} \end{vmatrix}.$$

By keeping $c_{33} \neq 0$ (the case when $c_{33}=0$ is not interesting) we shall get $\Delta_2=0$ when $c_{11}^2=-c_{12}c_{21}$. Therefore *there will be an invariant line passing through the origin and lying in the xy-plane, all of whose points are separately invariant.*

If the rank of Δ_2 is one all points of the xy-plane are invariant.

3. We shall now investigate the invariants of fluid motion expressed by a linearoid group. In the linearoid group expressing a fluid motion, under forces having a potential, the infinitesimal transformation Kf,

$$Kf = u\frac{\partial f}{\partial x} + v\frac{\partial f}{\partial y} + w\frac{\partial f}{\partial z},$$

where

$$\begin{cases} u = \phi_1 x + \phi_2 y + \phi_3, \\ v = \psi_1 x + \psi_2 y + \psi_3, \\ w = F_1 x + F_2 y + F_3, \end{cases} \tag{17}$$

$\phi_1, \phi_2, \ldots, F_3$ being functions of z only, must be of such a form that one of the following sets of conditions must be satisfied:[4]

Set I, in which $F_1=F_2=0$, consists of two subsets, which we shall denote by I_a, I_b.

[4] Trans. Am. Math. Soc., V. 1, pp. 347–352.

I_a. When $F_1=F_2=0$ and $\phi_1+\psi_2=0$, then

$$\begin{cases} \phi_1^2+\phi_2\psi_1=2\sigma=constant, \\ \phi_1\phi_3+\phi_2\psi_3+F_3\phi'_3=2\tau_1=constant, \\ \psi_1\phi_3+\psi_2\psi_3+F_3\psi'_3=2\tau_2=constant, \end{cases} \tag{18}$$

where ϕ'_3, ψ'_3 are the derivatives with respect to z, and where ϕ_1, ϕ_2, F_3 may be taken as arbitrary functions of z.

I_b. When $F_1=F_2=0$, and $\phi_2=\psi_1$, then

$$\begin{cases} \phi_2(\phi_1+\psi_2)=2\rho_2=constant, \\ \phi^2_1+\phi^2_2=2\rho_1=constant, \\ \phi^2_2+\psi^2_2=2\sigma_2=constant, \end{cases} \tag{19}$$

Where ϕ_1 and ψ_2 may be taken arbitrary functions of z, and the equations for ϕ_3, ψ_3, F_3 are of the same form as in (18).

If the fluid is incompressible we have further, $F_3=$constant in case I_a, and in case I_b we have

$$F_3=-\int(\phi_1+\psi_2)dz+constant.$$

Set II, in which $F_1\neq 0$, $F_2=0$ we have

$$\begin{cases} \phi_1=\alpha,\ \phi_2=\beta,\ \phi'_3=F_1+\dfrac{\epsilon-\alpha^2-\beta\gamma}{F_1}, \\ \psi_1=\gamma,\ \psi_2=\delta,\ \psi'_3=\dfrac{(\beta-\gamma)(\alpha+\delta)}{F_1}, \end{cases} \tag{20}$$

where α, β, γ, δ, ϵ are constants, and F_1, F_3 satisfy the differential equations,

$$\begin{cases} (\gamma-\beta)F_1+\dfrac{\gamma(\epsilon-\alpha^2-\beta\gamma)+\delta(\beta-\gamma)(\alpha+\delta)}{F_1} \\ \qquad +(\beta-\gamma)(\alpha+\delta)\dfrac{d}{dz}\left(\dfrac{F_3}{F_1}\right)=0, \\ \dfrac{\alpha(\epsilon-\alpha^2-\beta\gamma)+\beta(\beta-\gamma)(\alpha-\delta)}{F_1}+\dfrac{d}{dz}(F_1F_3) \\ \qquad +(\epsilon-\alpha_2-\beta\gamma)\dfrac{d}{dz}\left(\dfrac{F_3}{F_1}\right)-F_1F'_3=0, \end{cases} \tag{21}$$

where the accents denote derivatives with respect to z.

Let us now investigate the invariants corresponding to the above enumerated cases. In case I_a we shall get, by putting expressions (17) equal to zero, the equations

$$\left\{\begin{aligned} u &\equiv \phi_1 x + \phi_2 y + \phi_3 = 0, \\ v &\equiv \psi_1 x + \psi_2 y + \psi_3 = 0, \\ w &\equiv \quad . \qquad\qquad F_3 = 0. \end{aligned}\right. \tag{22}$$

By finding the roots of $F_3=0$ and substituting in the equations $u=0$, $v=0$, we shall get one of the following cases:

$$\left\{\begin{aligned} &\text{(a)}\quad \phi_1(z_k) = \phi_2(z_k) = \phi_3(z_k) = F_3(z_k) \\ &\qquad\qquad = \psi_1(z_k) = \psi_2(z_k) = \psi_3(z_k) = 0, \\ &\text{(b)}\quad \phi_3(z_k') = \psi_3(z_k) = F_3(z_k) = 0, \\ &\text{(c)}\quad \phi_3(z_k) \neq 0, \psi_3(z_k) \neq 0, \text{ or } \phi_3(z_k) \neq 0,\ \psi_3(z_k) = 0, \\ &\qquad\qquad\qquad\qquad \text{or } \phi_3(z_k) = 0,\ \psi_3(z_k) \neq 0. \end{aligned}\right. \tag{23}$$

where z_k is the root of $F_3=0$.

In case (a) there will be the planes

$$z=z_1, \quad z=z_2, \quad \ldots, z=z_k$$

which remain invariant during the motion, also every point in those planes will be separately invariant.

It may be remarked that if σ, τ_1, τ_2 in formula (18) are not zero, case (a) cannot take place.

In case (b) equations (22) will have a solution if

$$\begin{vmatrix} \phi_1(z_k) & \phi_1(z_k) \\ \psi_1(z_k) & \psi_2(z_k) \end{vmatrix} = 0.$$

This may happen only when $\sigma=0$, as equations (18) readily show. Therefore, *when* $\sigma=0$ *there will be invariant lines lying in the planes*

$$z=z_1, \quad \ldots, \quad z=z_k$$

and passing through the z-axis. Every point of those lines again, as before, will remain at rest.

In case (c) there will, as it is readily seen from equations (22), *be a discrete number of points which remain invariant during the entire motion.*

If the fluid is incompressible, in which case $F_3 = \text{constant}$, we shall have no invariant points unless $F_3 = 0$.

Consider now case I_b. Equations (22) will then take the form

$$\begin{cases} u \equiv \phi_1 x + \phi_2 y + \phi_3 = 0, \\ v \equiv \phi_2 x + \psi_2 y + \psi_3 = 0, \\ w \equiv F_3 = 0. \end{cases} \tag{24}$$

Here the same cases (a), (b), (c) may arise and be treated in the same way. Furthermore, when the fluid is incompressible there *may be* invariant configurations similar to those of a compressible fluid.

4. The case when $F_1 \neq 0$, $F_2 = 0$ will now be investigated. The invariant points of the fluid motion in this case will be given by the equations

$$\begin{cases} u \equiv \alpha x + \beta y + \phi_3 = 0, \\ v \equiv \gamma x + \delta y + \psi_3 = 0, \\ w \equiv F_1 x + F_3 = 0, \end{cases} \tag{25}$$

where $\alpha, \beta, \gamma, \delta, \phi_3, \psi_3, F_1, F_3$ are defined by equations (20), (21).

Solving equations (21) we find the following relationship between F_1 and F_3:

$$F_3 = \frac{c\, e^{fF_1^2} F_1^m}{(A_1 F_1^2 + A_2)^n}, \tag{26}$$

where A_1, A_2, f, m, n are constants depending upon $\alpha, \beta, \gamma, \delta, \epsilon$, and c is the constant of integration. And from equation (20) we get

$$\begin{cases} \phi_3 = c_1 \int \frac{F_1^{m+2}\, e^{fF_1^2}}{(A_1 F_1^2 + A_2)^{n+1}}\, dF_1 + C_2 \int \frac{F_1^{m+1}\, e^{fF_1^2}}{(A_1 F_1^2 + A_2)^{n+1}}\, dF_1, \\ \psi_3 = C_3 \int \frac{F_1^m e^{fF_1^2}}{(A_1 F_1^2 + A_2)^{n+1}}\, dF_1, \end{cases} \tag{27}$$

where c_1, c_2, c_3 are arbitrary constants.

From equation (26) we see that the function w has F_1 as a factor. If therefore we find the values of z which make $F_1=0$, and substitute those values in $u=0$ and $v=0$, then because of equations (27) we shall get

$$u=\alpha x+\beta y+K_1=0,$$
$$v=\gamma x+\delta y+K_2=0,$$

where K_1 and K_2 are arbitrary constants.

Now if the determinant

$$\Delta_1 \equiv \begin{vmatrix} \alpha & \beta \\ \gamma & \delta \end{vmatrix} \neq 0,$$

then for $K_1 \neq 0$ and $K_2 \neq 0$, we shall get p invariant points, one in each of the planes.

$$z=z_1, \ldots, z=z_p,$$

where $z_1, \ldots z_p$ are the roots of $F_1=0$.

If however, $\Delta_1=0$, then only for $K_1=K_2=0$ will there be invariant lines lying in the planes.

$$z=z_1, \ldots, z=z_p$$

and passing through the Z-axis.

Finally, denoting by w_1 the ratio $\frac{w}{F_1}$, we may find the invariant configurations by solving equations

$$u=0,\ v=0,\ w_1=0,$$

the Z-coördinates of whose points do not make $F_1=0$.

HYPERQUATERNIONS

By C. L. E. Moore

1. **Introduction.** In all discussions of Hamiltonian quaternions in three dimensions the 1-vector is taken as the fundamental geometric quantity. This is natural, since a definite vector is picked out by the form of the quaternion itself. Also when used to define rotations a vector is uniquely determined, *viz.*, the vector left invariant by the rotation. However when rotations are applied to a space of even dimensions there are no fundamental 1-vectors but there are fundamental 2-vectors[1], *viz.* the planes left invariant by the rotation. It seems to me, therefore, that the fundamental geometric quantity for the hyperquaternion should be the 2-vector which may be either simple or complex.

The system of units used in this paper is that of Lipschitz.[2] In n dimensions he takes the primary units

$$1,\ i_{12},\ i_{13},\ \ldots\ i_{1n},$$

$$\text{where } i_{kl} = -i_{lk},\ i_{12}^2 = i_{13}^2 = \ldots = i_{1n}^2 = -1,$$

and the units derived from them by the following laws of multiplication

$$i_{1m}i_{1n} = i_{mn},\ i_{1m}i_{1n}i_{1p} = i_{1mnp}.$$

[1] L. Schläfli. Theorie der vielfachen Kontinuität. Neue Denkschr. d. algem. Schweizer Gesellsch. 38, Zurich 1901. Published by J. H. Graf.

C. Jordan, Essai sur la géométrie à n dimensions. Bulletin Soc. Math. de France 3 (1875), p. 103.

C. L. E. Moore, Rotations in hyperspace, Proc. Amer. Acad. Arts and Sciences, Vol. 53, p. 651.

H. B. Phillips and C. L. E. Moore, Rotations in Even Dimensions, Proc. Amer. Acad., Vol. 55, p. 157.

When the last two papers were written we were not aware of the work of Schläfli and Jordan. They both obtained the result that in a space of $2n$ dimensions a rotation leaves n mutually completely perpendicular planes invariant and the corresponding theorem for space of odd dimensions. Jordan showed that the rotation could be resolved into rotations in these invariant planes.

C. Segre, Mehrdimensionale Raume, Encyclopädie der Math. Wiss. Band III, Heft. 7.

[2] Summen von Quadraten, Max Cohen and Sohn, Bonn 1886. A discussion of this system and others is found in the Study-Cartan article, Nombres Complexes; Encyclopedie des sciences math. tome 1, Vol. 1.

There are 2^{n-1} units in all. It is to be observed that the various units do not combine according to the same laws; for example, the primary units combine according to the anticommutative law, but this is not true of all units. Lipschitz defined a vector as

$$p=\lambda_0+\lambda_{12}i_{12}+\lambda_{13}i_{13}+\ldots.+\lambda_{1n}i_{1n} \tag{1}$$

and the hyperquaternion as

$$\alpha=\lambda_0+\Sigma\lambda_{pq}i_{pq}+\Sigma\lambda_{pqrs}i_{pqrs}+\Sigma\lambda_{pqrstu}i_{pqrstu}+\ldots. \quad \ldots. \tag{2}$$

where the coefficients satisfy the relations

$$\begin{aligned}\lambda_0\lambda_{pqrs} &= \lambda_{pq}\lambda_{rs}-\lambda_{pr}\lambda_{qs}+\lambda_{ps}\lambda_{qr} \\ \lambda_0^2\lambda_{pqrstu} &= \Sigma\lambda_{pq}\lambda_{rs}\lambda_{tu}\end{aligned} \tag{3}$$

where the summation extends over the various arrangements of $p, q, r, s, \ldots$ and the sign is determined by the permutation as usual. Similar relations hold for coefficients of a greater number of subscripts. It is to be noted that α is completely determined by the coefficients of the units of two subscripts and λ_0.

These hyperquaternions satisfy the usual laws of quaternions,

(1). The product of two hyperquaternions is again a hyperquaternion,

(2). The norm (sum of squares of the coefficients) of a product is the product of the norms,

(3). The conjugate of a product is the product of the conjugates taken in the reverse order.

A rotation is defined by

$$\alpha p\alpha_1^{-1}=q, \tag{4}$$

where p and q are vectors and α_1 is obtained from α by changing the sign of all terms which contain the subscript 1. Lipschitz also considered the set of units

$$i_pi_q=i_{pq}, \text{ where } i_p^2=i_q^2=-1$$

and showed that

$$\alpha_1=i_1^{-1}\alpha i_1$$

Using this set of units the vector (1) can be written

$$p=-(\lambda_0i_1+\lambda_{12}i_2+\ldots+\lambda_{1n}i_n)\,i_1=-vi_1\,.$$

Substituting in (4) we have

$$\alpha v i_1 i_1^{-1} \alpha i_1 = u i_1 .$$

From which

$$\alpha v \alpha^{-1} = u. \tag{5}$$

That is, defining the vector as

$$v = a_1 i_1 + a_2 i_2 + \ldots . + a_n i_n \ldots . \tag{6}$$

the operation (5) is a transformation which transforms vectors into vectors.

2. **Representation and transformation of planes.** If two such vectors p and q are mutiplied together according to the above laws of quaternion multiplication the product will contain a scalar part and a vector part. The coefficients of the vector part are seen to be the Plücker co-ordinates of the plane joining the two vectors[3] in the term containing that coefficient and hence the vector part of this product can be taken as the vector plane of the two 1-vectors. Since

$$\alpha p \alpha^{-1} \alpha q \alpha^{-1} = \alpha (pq) \alpha^{-1} = p^1 q^1,$$

we see that (15) is a plane transformation.

If two planes are multiplied together the product will consist of three parts. Thus representing the planes by P, Q,

$$PQ = A. + \Sigma A_{hk} i_{hk} + \Sigma A_{hklm} i_{hklm}.$$

The scalar part is obtained by multiplying units having the same subscripts together. The second term is obtained by multiplying together units which have a common figure in the subscript. This term is then obtained by multiplying the two planes according to the product $[\ ]_1$ discussed by Moore and Phillips.[4] The result there obtained was, if P and Q are unit planes and π_1 and π_2 are unit planes lying in the 4-space determined by P and Q and perpendicular to them, then

$$[PQ]_1 = \pi_1 \cos\Theta_2 + \pi_2 \cos\Theta_1$$

[3]The planes of two such vectors will always pass through the origin and the geometry of planes passing through a fixed point is simply isomorphic with the geometry of lines in a space of one lower dimension.

[4]Note on geometrical products, Proc. Nat. Acad. of Sciences, Vol. 5. This is what we called "star product," Proc. Amer. Acad. Vol. 55.

where Θ_1 and Θ_2 are the angles intercepted in π_1 and π_2 between P and Q. This is the analog of the Hamilton vector product of two vectors. If this product vanishes P and Q are either coincident or completely perpendicular. The product $[PQ]_1$ becomes a simple 2-vector or plane in two cases. If P and Q are simply perpendicular, that is P contains one vector perpendicular to Q and Q contains one vector perpendicular to P. In this case one of the angles Θ is $\pi/2$. It is also seen that this is a simple plane because the scalar term will vanish in this case and from (3) we have

$$A_{pq}A_{rs} - A_{pr}A_{qs} + A_{ps}A_{qr}' = 0 \tag{7}$$

which is the condition that the 2-vector be a plane. This product will vanish also when P and Q lie in the same three space, for in that case the last term of the product will vanish and from (7) equation (3) will again hold. If P and Q coincide the product will reduce to the scalar term, while if P and Q are completely perpendicular it will reduce to the last term.

3. **Canonical form of the hyperquaternion.** From (3) it is seen that the coefficients λ_{pqrs} are proportional to the coefficients in the outer or cross product of the 2-vector part of the hyperquaternion with itself. If then we denote this 2-vector part by P we can write α in the form

$$\alpha = \lambda_0 + P + \frac{1}{\lambda_0 2!} P \times P + \frac{1}{\lambda_0^2 3!} P \times P \times P + \ldots \tag{8}$$

The 2-vector P is in general a complex. If this is a simple plane then the terms $P \times P$, $P \times P \times P \ldots$ all vanish. In a space of $2m$ or $2m+1$ dimensions a complex 2-vector can be resolved into the sum of m mutually completely perpendicular planes. This resolution is in general unique.[5] Hence, writing

$$P = \rho_1 P_1 + \rho_2 P_2 + \ldots + \rho_m P_m ,$$

where $P_1, P_2, \ldots P_m$ are mutually completely perpendicular unit planes, we have

[5] Rotations in hyperspace, note 1.

$$\alpha = \lambda_0 + P + \frac{1}{\lambda_0} \Sigma \rho_h \rho_k P_h \times P_k + \frac{1}{\lambda_0^2} \Sigma \rho_h \rho_k \rho_l P_h \times P_k \times P_l + \ldots \qquad (9)$$

Now the product

$$(\lambda_0 + \rho_1 P_1)(\lambda_0 + \rho_2 P_2) = \lambda_0^2 + \lambda_0(\rho_1 P_1 + \rho_2 P_2) + \rho_1 \rho_2 P_1 \times P_2 ,$$

since the 2-vector arising from multiplying P_1 by P_2 vanishes, P_1 and P_2 being completely perpendicular. The product

$$(\lambda_0 + \rho_1 P_1)(\lambda_0 + \rho_2 P_2)(\lambda_0 + \rho_3 P_3) = \lambda_0^3 + \lambda_0^2(\rho_1 P_1 + \rho_2 P_2 + \rho_3 P_3) + (\rho_1 \rho_2 P_1 \times P_2 + \rho_1 \rho_3 P_1 \times P_3 + \rho_2 \rho_3 P_2 \times P_3) + \rho_1 \rho_2 \rho_3 P_1 \times P_2 \times P_3 .$$

This follows immediately except for the 2-vector that might arise from such products as $P_1(P_2 \times P_3)$ . . This is the product $[\ ]_2$ of Moore and Phillips and it was shown that this product vanishes when the two spaces are completely perpendicular, which is the case with all these products. It is at once evident that the product of more factors follows the same formula and hence the general hyperquaternion can be written in the factored form,

$$\alpha = \frac{1}{\lambda_0^{m-1}} (\lambda_0 + P_1)(\lambda_0 + \rho_2 P_2) \ldots . (\lambda_0 + \rho_m P_m) . \qquad (10)$$

Obviously these factors are all commutative. The factorization is in general unique. The factors $\lambda_0 + \rho_k P_k$ can be factored into linear factors and hence α can be expressed as the product of 1-vectors.[6] This factorization, however, is not unique, and only in very special cases is it commutative.

4. **Hyperquaternions in 4-space.** In 4-space the hyperquaternion has a single unit with four subscripts, i_{1234}. The square of this unit, is unity and it is commutative with all other units. We can then write any hyperquaternion

$$A = a_0 + a_{12} i_{12} + a_{13} i_{13} + \ldots + a_{34} i_{34} + aI$$

in the form

$$A = \alpha + I\beta ,$$

[6] Th. K. Vahlen, Über Bewegungen und complexe Zahlen, Math. Ann., 55.

where

$$\alpha = a_0+a_{12}i_{12}+a_{13}i_{13}+a_{23}i_{23},$$
$$\beta = a-a_{34}i_{12}+a_{24}i_{13}-a_{14}i_{23},$$
$$I = i_{1234}.$$

α and β are Hamiltonian quaternions. The hyperquaternion is then expressed as a biquaternion where the new unit I is commutative with all other units and satisfies the relation $I^2=1$. The relation which the coefficients satisfy if A is a hyperquaternion can now be written

$$S(\alpha\bar{\beta})=0.$$

The hypercomplex number, whether it is a hyperquaternion or not, can be written as a biquaternion. The product of two such complex numbers is

$$(\alpha+I\beta)(\gamma+I\delta)=\alpha\gamma+\beta\delta+I(\alpha\delta+\beta\gamma).$$

If this product is commutative (since all the scalar parts are already commutative with all the vector parts)

$$\alpha_1\gamma_1+\beta_1\delta_1=\gamma_1\alpha_1+\delta_1\beta_1$$
$$\alpha_1\delta_1+\beta_1\gamma_1=\delta_1\alpha_1+\gamma_1\beta_1$$

where α_1, β_1, γ_1, δ_1 indicate the vector parts of the corresponding quaternions. Adding and subtracting these two equations we have

$$(\alpha_1+\beta_1)(\gamma_1+\delta_1)=(\gamma_1+\delta_1)(\alpha_1+\beta_1),$$
$$(\alpha_1-\beta_1)(\gamma_1-\delta_1)=(\gamma_1-\delta_1)(\alpha_1-\beta_1). \tag{11}$$

Thus the two original complex numbers will be commutative if the two pairs of Hamiltonian quaternions $\alpha_1+\beta_1$, $\gamma_1+\delta_1$ and $\alpha_1-\beta_1$, $\gamma_1-\delta_1$ are commutative. These will be commutative only when these vectors are proportional. Hence

$$\begin{aligned} a_{12}+a_{34}&=\rho(b_{12}+b_{34}),\\ a_{13}-a_{24}&=\rho(b_{13}-b_{24}),\\ a_{14}+a_{23}&=\rho(b_{14}+b_{23}), \end{aligned} \tag{12}$$

and

$$\begin{aligned} a_{12}-a_{34}&=\rho_1(b_{12}-b_{34}),\\ a_{13}+a_{24}&=\rho_1(b_{13}+b_{24}),\\ a_{14}-a_{23}&=\rho_1(b_{14}-b_{23}). \end{aligned} \tag{13}$$

Solving these equations for the b's we have

$$b_{12}=\lambda a_{12}+\mu a_{34},$$
$$b_{13}=\lambda a_{13}-\mu a_{24},$$
$$b_{14}=\lambda a_{14}+\mu a_{23},$$
$$b_{23}=\lambda a_{23}+\mu a_{14},$$
$$b_{24}=\lambda a_{24}-\mu a_{13},$$
$$b_{34}=\lambda a_{34}+\mu a_{12}.$$

From which we see at once that A and B will be commutative if

$$B=\rho+\lambda A+\mu IA+\sigma I \tag{14}$$

where ρ, λ, μ, σ are constants. If B is a hyperquaternion the coefficients must satisfy (3), and consequently the constants are not independent.

These are the general conditions of *commutativity*, but from equation (11) we see that if $\alpha_1=\beta_1$ there is only one relation to be satisfied and this will be satisfied for any complex number for which $\gamma_1=-\delta_1$. That is, any complex number for which $\alpha_1=\beta_1$ is commutative with any one for which $\gamma_1=-\delta_1$. From the rules for the product of I with the other units it is at once seen that $\alpha_1=\beta_1$ is equivalent to the relation $A=-IA$, and that $\gamma_1=-\delta_1$ is equivalent to the relation $B=IB$. When the latter relation holds, the complex number is said to be self-complementary, and when the former holds the number is said to be anti-self-complementary. Hence, *in 4-space any self-complementary number is commutative with any anti-self-complementary one.*[7]

5. From (14) we can determine the planar complex numbers (those for which the 2-vector part is a plane) which are commutative with A. If the 2-vector part of $\lambda A+\mu IA$ is a plane,

$$(\lambda a_{12}+\mu a_{34})(\lambda a_{34}+\mu a_{12})-(\lambda a_{13}-\mu a_{24})(\lambda a_{24}-\mu a_{13})$$
$$+(\lambda a_{14}+\mu a_{23})(\lambda a_{23}+\mu a_{14})=0.$$

Consequently there are in general two such planar complex numbers. It is not difficult to show that if one of these is $\lambda_1 A+\mu_1 IA$) the

[7] See rotations in space of even dimensions, note 1.

other will be $I(\lambda_1 A+\mu_1 IA)$. If P is a plane, then IP is the plane completely perpendicular to it. Hence, the two planes commutative with a complex number are completely perpendicular. Also,

$$A=[\lambda_1(\lambda_1 A+\mu_1 IA)-\mu_1(\mu_1 A+\lambda_1 IA)]/(\lambda_1^2-\mu_1^2);$$

consequently this expresses the 2-vector part of A as the sum of two completely perpendicular planes.

If $\alpha_1=\beta_1$ the last equation of (11) is satisfied, and consequently

$$b_{12}+b_{34}=\rho a_{12}, b_{13}-b_{24}=\rho a_{13}, b_{14}+b_{23}=\rho a_{14}.$$

Hence, the complex numbers commutative with A are

$$B=b_0+(\rho a_{12}-b_{34})i_{12}+(\rho a_{13}+b_{24})i_{13}+(\rho a_{14}-b_{23})i_{14}$$
$$+b_{23}i_{23}+b_{24}i_{24}+b_{34}i_{34}+bI.$$

If this is planar—

$$(\rho a_{12}-b_{34})b_{34}-(\rho a_{13}+a_{24})b_{24}+(\rho b_{14}+b_{34})b_{23}=0,$$

and consequently there are ∞^2 of these planar numbers commutative with A. It is not difficult to show that the 2-vector part of B can be expressed as a linear function of pairs of these planes which are completely perpendicular. Similar argument applies to the case $\alpha_1=-\beta_1$. If the complex number satisfies (3) we have: *If A is self-complementary or anti-self-complementary, it can be expressed in ∞^2 ways, as the sum of completely perpendicular planar hyperquaternions.*

6. **Interpretation of the coefficients.** When used as a transformer the hyperquaternion can be divided by a constant without affecting the transformation. We shall then write it in the canonical form with $\rho_0=1$,

$$A=1+\rho_1 P_1+\rho_2 P_2+\rho_1\rho_2 I.$$

Now choose two perpendicular 1-vectors in each of the planes P_1, P_2,

$$p_1p_2=P_1, \quad p_3p_4=P_2.$$

Then

$$Ap_1A^{-1}=\frac{1-\rho_1^2}{1+\rho_1^2}p_1+\frac{2\rho_1}{1+\rho_1^2}p_2,$$

from which it is seen that if $2\phi_1$ is the angle through which p_1 is rotated then,

$$\rho_1 = tan\ \phi_1.$$

Likewise,

$$\rho_2 = tan\ \phi_2,$$

where ϕ_2 is the angle through which vectors in P_2 are rotated. A unit planar hyperquaternion can then be written

$$P = cos\ \phi_1 + P_1\ sin\ \phi_1,$$

and the general one can be written—

$$A = (cos\ \phi_1 + P_1\ sin\ \phi_1)(cos\ \phi_2 + P_2\ sin\ \phi_2).$$

Expanding $sin\ \phi_1$ and $cos\ \phi_1$ in P, and remembering that $P^2 = -1$,

$$cos\ \phi_1 + P_1\ sin\ \phi_1 = 1 + P_1\phi_1 + \frac{(P_1\phi_1)^2}{2!} + \frac{(P_1\phi_1)^3}{3!} + \ \ldots\ = e^{P_1\phi_1}.$$

Then A can be written—

$$A = e^{P_1\phi_1} \cdot e^{P_2\phi_2},$$

and since P_1 and P_2 are commutative

$$A = e^{P_1\phi_1} \cdot e^{P_2\phi_2} = e^{P_1\phi_1 + P_2\phi_2} = e^{P}, \tag{15}$$

where $P = P_1\phi_1 + P_2\phi_2$.

This is the square root if the formula which Phillips and Moore[8] obtained for the exponential form of the dyadic representing a rotation and the argument establishing the uniqueness of the exponent can easily be paralleled.

The complex P can be written as the sum of the two complexes

$$P = \tfrac{1}{2}(P - IP) + \tfrac{1}{2}(P + IP),$$

the first of which is self-complementary and the second anti-self-complementary. Since these two are commutative,

$$A = e^{\frac{1}{2}(P - IP)} \cdot e^{\frac{1}{2}(P + IP)}$$

Hence, *every hyperquaternion in 4-space can be expressed uniquely as the product of a self-complementary and an anti-self-complementary one.*

[8]Proc. Amer. Acad., Vol. 55.

7. **Subgroups.** Any self-complementary hyperquaternion can be written

$$A = a_0 + a_1(i_{12} + i_{34}) + a_2(i_{13} - i_{24}) + a_3(i_{14} + i_{23}) + aI.$$

By actual multiplication it is seen that the product of two such numbers is again self-complementary. The same is true of the anti-self-complementary numbers. Hence, the self-complementary and the anti-self-complementary quaternions form subgroups. These subgroups are self-conjugate. For factoring the hyperquaternion B into its self-complementary and anti-self-complementary factors, $B = \phi\phi^1$ and transforming A by it, we have

$$B^{-1}AB = \phi^{-1}\phi^{1-1}A\phi\phi^1 = \phi^{-1}A\phi,$$

since ϕ^1 and A are commutative, one being self-complementary and the other anti-self-complementary. But ϕ^{-1}, A_1, ϕ, are all self-complementary, and hence the subgroup A transforms into itself. These are four parametered subgroups.

Also such numbers as

$$H = a_o + a_{12}i_{12} + a_{13}i_{13} + a_{23}i_{23},$$

form a four parametered subgroup. This is the ordinary Hamiltonian quaternion, and is what we have called "planar." There are other sets of planar hyperquaternions which do not form a sub-group; for example:

$$K = a_o + a_{12}i_{12} + a_{13}i_{13} + a_{14}i_{14}.$$

The product of two numbers of type K is obviously not one of type K. The vector part of H is the sum of three planes lying in the 3-space determined by i_1, i_2, i_3, while that of K is the sum of three planes having a line in common. If we transform H and K by any hyperquaternion B, we have

$$B^{-1}HB = H^1,$$
$$B^{-1}KB = K^1,$$

where H^1 and K^1 belong to the same set as H and K. The set K is what Lipschitz used for vectors, and the hyperquaternion was built so as to transform vectors into vectors. If p_1, p_2, p_3, p_4, are four mutually perpendicular vectors then, the two sets

$$a_o + a_{12}p_{12} + a_{13}p_{13} + a_{23}p_{23},$$
$$a_o + a_{12}p_{12} + a_{13}p_{13} + a_{14}p_{14},$$

have the same properties as H and K. For any hyperquaternion can be expressed in term of these vectors instead of the vectors i_1, i_2, i_3, i_4.

The two parametered subgroups are simply isomorphic with the complex variable. These are numbers of the type

$$c = a_0 + a_1 P_1,$$

where P_1 is a unit plane.

8. **Geometric representation of hyperquaternions in 4-space.** Equation (3) suggests that hyperquaternions can be represented in a homogeneous space of seven dimensions, and the geometry will be analogous to the Plücker line geometry in three dimensions. However, here I shall use a non-homogeneous space of eight dimensions, and then

$$\Omega(a) = a_0 a - a_{12}a_{34} + a_{13}a_{24} - a_{14}a_{23} = 0 \tag{16}$$

will represent a hypercone, and only the vectors of this cone will represent hyperquaternions. Through each vector of this cone will pass two linear spaces of four dimensions which lie on Ω. The linear spaces of one type are transformed by any hyperquaternion into linear spaces of the same type. These correspond to special linear congruences of lines.

If the product $B^{-1}A$ is to be planar it is only necessary for the coefficient of I to vanish. This gives

$$\Omega(ab) = a_0 b + b_0 a - a_{12}b_{34} - a_{34}b_{12} + a_{13}b_{24} + a_{24}b_{13} - a_{14}b_{23} - a_{23}b_{14} = 0. \tag{17}$$

This is the polar of Ω and corresponds to the condition that two lines intersect. Equation (17) is that of a tangent hypercone to Ω, and therefore cuts it in a cone with a rectilinear vertex. Hence all the hyperquaternions B which satisfy the relation that $A^{-1}B$ is planar lie on the cone in which the tangent hyperplane at A cuts Ω. If $\lambda A + \mu B$ is to be a hyperquaternion

$$\lambda^2 \Omega(a) + \lambda\mu\, \Omega(ab) + \mu^2 \Omega(b) = 0.$$

But $\Omega(a) = \Omega(b) = 0$ since A and B are hyperquaternions. Then (17) is the condition that any linear combination of A and B is a hyperquaternion. Hence, *if $A^{-1}B$ is planar any linear com-*

bination of A and B is a hyperquaternion. This is the condition that A and B lie in a plane of Ω. Since

$$(\lambda A^{-1}+\mu B^{-1})\ (\lambda A+\mu B)=\lambda^2+\mu^2+\lambda\mu(A^{-1}B+B^{-1}A)$$

is planar, it follows that in a plane of Ω the quotient of any two is always planar, and since the plane of $A^{-1}B$ coincides with that of $B^{-1}A$ these quotients are all coplanar. Likewise if A, B, C lie in a 3-space of Ω, that is, if

$$\Omega(ab)=\Omega(ac)=\Omega(bc)=0,$$

then

$$A^{-1}(\lambda A+\mu B+\nu C)=\lambda+\mu A^{-1}B+\nu A^{-1}C$$

is planar, and consequently the planes of $A^{-1}B$ and $A^{-1}C$ must have a line in common. Hence the quotient of any quaternion lying in this 3-space by A will give planar quaternions whose planes have a line in common. Similarly, if A, B, C, D lie a 4-space on Ω, then any hyperquaternion in this 4-space divided by A will give a planar one; the planes of all these quotients either lie in a 3-space or have a line in common. These correspond to the two types of 4-space on Ω.

By multiplying by an arbitrary hyperquaternion, those lying in a linear space on Ω are transformed into those lying in a linear space. Also, any 4-space lying on Ω is transformed into a 4-space of the same kind. For if $\lambda A+\mu B+\nu C+\rho D$ is a hyperquaternion for all values of the parameters, then

$$\Gamma^{-1}(\lambda A+\mu B+\nu C+\rho D)\,\Gamma$$

is a hyperquaternion for all values of the parameters. If the planes of $A^{-1}B$, $A^{-1}C$, $A^{-1}D$, lie in the same 3-space, then

$$\Gamma^{-1}A^{-1}B\,\Gamma,\ \Gamma^{-1}A^{-1}C\,\Gamma,\ \Gamma^{-1}A^{-1}D\,\Gamma,$$

will necessarily lie in the same 3-space. Likewise if the planes of the first three have a line in common the second three will have, also.

If A is planar, $a=0$ and

$$\Omega_1(a)=a_{12}a_{34}-a_{13}a_{24}+a_{14}a_{23}=0.$$

Through each vector of this type will pass two kinds of 4-space, one of type H and the other of type K. The transformation by Γ

will leave Ω_1 invariant, and will transform linear space of type H or K into spaces of the same type.

If A is a hyperquaternion, A^2 will not lie in a plane with A (that is, $\lambda A+\mu A^2$ will not be a hyperquaternion for all values of the parameters) unless $A^{-1}A^2$ is planar. *A planar hyperquaternion is then the only one which is coplanar with its powers.* Through any planar hyperquaternion passes a 4-space of type H. The hyperquaternions of this 4-space are simply isomorphic with Hamiltonian quaternions. In this space A and A^2 will lie in a space passing through the axis of reals.[9] If A and B both lie in H then the product $A(\lambda A+\mu AB)$ will lie in a plane determined by B and AB. For

$$A^2=\rho+\sigma A \quad (\rho \text{ and } \sigma \text{ being scalars}),$$

and therefore

$$A(\lambda A+\mu AB)=\xi B+\mu AB,$$

which shows that by multiplication by A on the right every quaternion is rotated in an invariant plane, that is, through every quaternion passes a plane which is left invariant by right-hand multiplication. It is easy to see that the same is true for left-hand multiplication.[10]

9. **The linear complex.** The linear complex will be defined as usual as a linear relation connecting the coördinates. This is represented in the 8-space as a hyperplane which will cut Ω in a quadric cone of six dimensions. It will cut the quadric Ω_1 in a cone of five dimensions. When the hyperplane is tangent to Ω the complex is called *special* and is then the locus of all hyperquaternions whose quotients by A (the point of contact) areplanar. A pencil of complexes determines a pair of special complexes. Given any complex A, then any hyperquaternion α will determine with A a pencil of complexes and consequently a second hyperquaternion β (the vertex of the second special complex of the pencil $A\alpha$). The hyperquaternion β is then called the polar of α with respect to A. A complex can be expressed as the sum of

[9] Phillips, Application of Quaternions to Four Dimensions. The Johns Hopkins University Circular, January, 1905.

[10] See Study-Cartan, Encyclopédie des Sciences Math., Tome 1, Vol. 1, p. 452.

special complexes or quaternions. In fact, any complex can be written in the form

$$a_0+\Sigma a_{kl}i_{kl}+aI$$

where the coefficients are arbitrary and this can be written in the form

$$\alpha+I\beta.$$

Two complexes are said to be in involution if the product $A^{-1}B$ does not contain the unit I. This is the case if

$$\Omega(ab)=0.$$

10. **Hyperquaternions for any hyperspace.** From (9), if we choose the axes by pairs in the mutually perpendicular planes into which the complex of the hyperquaternion can be resolved, the hyperquaternion will contain only one term of order, m, the order of the space being $2m$ or $2m+1$. It is obvious that the hyperquaternion is commutative with the planar ones whose planes coincide with one of the above planes. Also, if the order of the space is $2m+1$, there is a 1-vector commutative with the hyperquaternion, *viz.*, the 1-vector which is perpendicular to each of the planes into which the hyperquaternion is resolved. In higher space we have the same exponential form as in 4-space,

$$A=e^{\phi_1P_1+\phi_2P_2+\ \cdots\ +\phi_mP_m} \tag{18}$$

where ϕ_k is the half angle through which vectors in the plane P_k are rotated by the transformation $A^{-1}P_mA$.

If the hyperquaternions

$$A=a_0+P+\frac{1}{2!}P\times P+\frac{1}{3!}P\times P\times P+\ \cdots$$

$$B=b_0+Q+\frac{1}{2!}Q\times Q+\frac{1}{3!}Q\times Q\times Q+\ \cdots$$

are commutative it is necessary and sufficient that P and Q be commutative, for if $PQ=QP$ then $Q(P\times P)=(P\times P)Q$, and likewise for the products of P's and Q's of higher order. The commutativity of P and Q requires that the vector part of PQ vanish.

That is,—

$$[PQ]_1 = 0.$$

If, now, we write

$$P = \rho_1 P_1 + \rho_2 P_2 + \ldots + \rho_m P_m = \rho_1 p_1 p_2 + \rho_3 p_3 p_4 + ,$$
$$Q = b_{12} p_1 p_2 + b_{13} p_1 p_3 + \ldots\ldots$$

where p_1 and p_2 are perpendicular vectors in P_1, etc. The product $[PQ]_1$ vanishes if

$$\begin{aligned} \rho_1 a_{13} + \rho_2 a_{24} &= 0, \\ \rho_1 a_{23} + \rho_2 a_{14} &= 0, \\ -\rho_1 a_{24} + \rho_2 a_{13} &= 0, \\ \rho_1 a_{14} - \rho_2 a_{23} &= 0; \end{aligned}$$

consequently,—

$$\frac{a_{13}}{a_{24}} = -\frac{a_{24}}{a_{13}}, \quad \frac{a_{23}}{a_{14}} = -\frac{a_{14}}{a_{23}};$$

and, since the coefficients are all real, it follows that

$$a_{13} = a_{14} = a_{23} = a_{24} = 0.$$

Hence, *if A and B are commutative they can be expressed in terms of the same set of completely perpendicular planes.*

If in (18) two of the ϕ's are equal (say $\phi_1 = \phi_2$), then in the 4-space $P_1 \times P_2$ the hyperquaternion is of the self-complementary type.

EXPLICIT DETERMINATION OF COTES' COEFFICIENTS FOR POLYNOMIAL AREA

By GEORGE RUTLEDGE

1. **Introduction.** Very early in the history of the calculus methods of approximate integration consisting essentially in the substitution for the function to be integrated of an approximating polynomial function of low degree were developed. In 1722, the astronomer Cotes, a co-worker with Newton, computed (for small values of n) the coefficients which bear his name and which are still in practical use. The familiar prismoidal formula and Simpson's Rule are special cases of Cotes' more general formulas.

The expressions for Cotes' coefficients (restricting them to even order) which are current in books[1] on analysis are the equivalent of the following:

$$K_{2n,\,i} = \tfrac{1}{2} \int_{-1}^{+1} \frac{\phi(t)\,dt}{\phi'(t_i)(t-t_i)}, \tag{1}$$

where $t_i = \dfrac{i}{n}$, and $\phi(t) = \prod_{i=-n}^{+n} (t-t_i)$, $(i = -n, \ldots, o, \ldots, +n)$.

If $P^{[2n]}(x)$ is that polynomial of degree $2n$ (at most) which is determined by the $2n+1$ points,

$$(-nh, y_{-n}), \ldots, (-h, y_{-1}), (o, y_o), (h, y_1), \ldots, (nh, y_n), \tag{2}$$

then Cotes' coefficients (of even order) satisfy the relation,

$$\int_{-nh}^{+nh} P^{[2n]}(x)\,dx = 2nh \left[K_{2n,-n}\, y_{-n} + \ldots + K_{2n,\,o} y_o + \ldots + K_{2n,\,n} y_n \right], \tag{3}$$

1 See *Jordan, Cours d'Analyse*, 2d ed., v. 2., p. 123. For an extended review of the results of Cotes, Gauss, Jacobi, Tchébychef, and others, see *Radau, Étude sur les formules d'approximation servent à calculer la valuer numérique d'une intégrale définie, Journal de mathématiques*, (3) 6, p. 283 (1880).

See also *Edinburgh Mathematical Tracts No. 2, Interpolation and Numerical Integration*, by *David Gibb*, G. Bell and Sons, London, 1915.

independently of the y's and of h, or more generally the relation,

$$\int_a^b P^{[2n]}(x)\,dx = (b-a)\left[K_{2n,-n}\,y_{-n} + \ldots\ldots + K_{2n,0}\,y_0 + \ldots\ldots + K_{2n,n}\,y_n\right], \qquad (4)$$

where the y's are the values of $P^{[2n]}(x)$ at equally spaced intervals from a to b.

For $n=1$, formula (4) becomes the prismoidal formula.

In this paper we shall obtain explicit expressions for Cotes' coefficients of even order in the form of finite series. The purpose of the restriction to even order is explained in the next section.

2. **Invariant Area.** The $2n+1$ points, (2), clearly determine a polynomial curve of degree $2n$ (at most). Let us call this curve, as in the previous article, $P^{[2n]}(x)$. These same points determine a set of polynomial curves of degree $2n+1$ with arbitrary parameter, μ. This parameter may mean, for example, the slope of the curve at (o, y_o). Let us call an arbitrarily chosen polynomial of this set, $P^{[2n+1]}(x, \mu)$. Then,

$$y = F^{[2n+1]}(x,\mu) = P^{[2n+1]}(x,\mu) - P^{[2n]}(x) \qquad (5)$$

is a polynomial curve of degree $2n+1$ which crosses the x-axis at the points, $x = -nh, \ldots\ldots, o, \ldots\ldots, nh$. Therefore

$$F^{[2n+1]}(x,\mu) = kx(x^2-h^2)(x^2-4h^2)\ldots\ldots(x^2-n^2h^2).$$

Since $F^{[2n+1]}(x,\mu)$ involves only odd powers of x,

$$\int_{-nh}^{+nh} F^{[2n+1]}(x,\mu)dx = o,$$

and therefore

$$\int_{-nh}^{+nh} P^{[2n+1]}(x,\mu)\,dx = \int_{-nh}^{+nh} P^{[2n]}(x)\,dx, \qquad (6)$$

independently of μ.

This invariant area property of a set of polynomial curves of odd degree is well known in the case of cubic[3] polynomial curves through three points equally spaced as to abscissa, by

[3] See *G. H. Hardy, Pure Mathematics*, Cambridge University Press, Cambridge, 1908, p. 295; also *Woods and Bailey, Analytic Geometry and Calculus*, Ginn & Co., Boston, 1917, p. 419.

virtue of which case Simpson's rule gives exact results for a cubic polynomial, although its derivation is commonly based on the quadratic polynomial. The generalization has not come to the author's attention.

In view of the fact that Cotes' formulas of a given even order serve to express areas under polynomial curves of both this even and the next higher odd degree it seems best to treat Cotes' coefficients of even order separately.

3. **Determinant Expressions for Cotes' Coefficients.** From the fact that formula (3) evaluates exactly,

$$\int_{-n}^{+n} x^2\,dx,\quad \int_{-n}^{+n} x^4,\,dx,\ldots\ldots,\quad \int_{-n}^{+n} x^{2n}dx,$$

we have the following linear equations in the coefficients,[3] $K_{2n,i}$:

$$\begin{aligned}
K_{2n,1}+2^2K_{2n,2}+3^2K_{2n,3}+\ldots\ldots+n^2K_{2n,n} &= \frac{n^3}{3}\cdot\frac{1}{2n}\\
K_{2n,1}+2^4K_{2n,2}+3^4K_{2n,3}+\ldots\ldots+n^4K_{2n,n} &= \frac{n^5}{5}\cdot\frac{1}{2n}\\
K_{2n,1}+2^6K_{2n,2}+3^6K_{2n,3}+\ldots\ldots+n^6K_{2n,n} &= \frac{n^7}{7}\cdot\frac{1}{2n}\\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
K_{2n,1}+2^{2n}K_{2n,2}+3^{2n}K_{2n,3}+\ldots+n^{2n}K_{2n,n} &= \frac{n^{2n+1}}{2n+1}\cdot\frac{1}{2n}
\end{aligned}\qquad (7)$$

The determinant of this system of equations is

$$D=\begin{vmatrix}
1 & 2^2 & 3^2 & \ldots\ldots & n^2\\
1 & 2^4 & 3^4 & \ldots\ldots & n^4\\
1 & 2^6 & 3^6 & \ldots\ldots & n^6\\
\ldots & \ldots & \ldots\ldots & \ldots & \ldots\\
\ldots & \ldots & \ldots\ldots & \ldots & \ldots\\
\ldots & \ldots & \ldots\ldots & \ldots & \ldots\\
\ldots & \ldots & \ldots\ldots & \ldots & \ldots\\
1 & 2^{2n} & 3^{2n} & \ldots\ldots & n^{2n}
\end{vmatrix} = n!\,3!\,5!\ldots\ldots\overline{2n-1}!\,[4] \qquad (8)$$

[3] The fact that $K_{2n,-1}=K_{2n,1}$ and that $K_{2n,0}=1-2\sum_{i=1}^{n}K_{2n,i}$ makes it possible to determine the $2n+1$ K's from these n linear equations.

[4] The evaluation is by reduction to Vandermonde's determinant.

4. **Evaluation of the Determinants.** If the equations (7) are now solved by Cramer's Rule, it may be noted that the cofactors of the elements of the i^{th} column of the numerator in the determinant expression for $K_{2n,i}$ are reducible to generalized[8] Vandermonde determinants of a particular type. This renders it possible (by an elaborate computation) to obtain the following expression for $K_{2n,i}$. Placing

$$G_{2n,i}=(-1)^{i+1}\frac{n!\,(n-1)!}{(n+i)!\,(n-i)!}, \tag{9}$$

$$K_{2n,i}=G_{2n,i}\frac{1}{i^2}\left\{\frac{n^3}{3}-\frac{n^5}{5}\overset{(i)}{\Sigma}\frac{1}{r^2}+\frac{n^7}{7}\overset{(i)}{\Sigma}\frac{1}{r^2s^2}-\cdots.\right.$$
$$\left.+(-1)^{n+1}\frac{n^{2n+1}}{2n+1}\frac{i^2}{(n!)^2}\right\}, \tag{10}$$

where $\overset{(i)}{\Sigma}\frac{1}{r^2}$ denotes the sum of the squared reciprocals of the first n integers, excepting i, $\overset{(i)}{\Sigma}\frac{1}{r^2s^2}$ denotes the sum of products of these squared reciprocals two at a time, etc.

For purposes of convenience in computation and for theoretical purposes, expression (10) may be transformed into an expression in the squared reciprocals of the first n integers, *not excepting* i, as follows:

We note that

$$\overset{(i)}{\Sigma}\frac{1}{r^2}=\Sigma\frac{1}{r^2}-\frac{1}{i^2},$$

$$\overset{(i)}{\Sigma}\frac{1}{r^2s^2}=\Sigma\frac{1}{r^2s^2}-\frac{1}{i^2}\overset{(i)}{\Sigma}\frac{1}{r^2}=\Sigma\frac{1}{r^2s^2}-\frac{1}{i^2}\Sigma\frac{1}{r^2}+\frac{1}{i^4},$$

$$\overset{(i)}{\Sigma}\frac{1}{r^2s^2t^2}=\Sigma\frac{1}{r^2s^2t^2}-\frac{1}{i^2}\overset{(i)}{\Sigma}\frac{1}{r^2s^2}=\Sigma\frac{1}{r^2s^2t^2}-\frac{1}{i^2}\Sigma\frac{1}{r^2s^2}+\frac{1}{i^4}\Sigma\frac{1}{r^2}-\frac{1}{i^6},$$

. . . . . .

[8] See *Pascal, Die Determinanten*, Leipzig, 1900, p. 131.

Therefore

$$K_{2n,i} = G_{2n,i}\frac{1}{i^2}\left[\frac{n^3}{3} - \frac{n^5}{5}\left\{\Sigma\frac{1}{r^2} - \frac{1}{i^2}\right\} + \frac{n^7}{7}\left\{\Sigma\frac{1}{r^2s^2} - \frac{1}{i^2}\Sigma\frac{1}{r^2} + \frac{1}{i^4}\right\} - \ldots\right]. \quad (11)$$

In this expression we may collect like powers of $\frac{1}{i^2}$, and writing,

$$\begin{aligned} R'_n &= \left\{\frac{n^3}{3} - \frac{n^5}{5}\Sigma\frac{1}{r^2} + \frac{n^7}{7}\Sigma\frac{1}{r^2s^2} - \frac{n^9}{9}\Sigma\frac{1}{r^2s^2t^2} + \ldots. + (-1)^{n+1}\frac{n^{2n+1}}{2n+1}\Sigma\frac{1}{r^2s^2\ldots.}\right\}, \\ R''_n &= \left\{\frac{n^5}{5} - \frac{n^7}{7}\Sigma\frac{1}{r^3} + \frac{n^9}{9}\Sigma\frac{1}{r^2s^2} - \ldots\ldots\ldots\right\}, \\ R'''_n &= \left\{\frac{n^7}{7} - \frac{n^9}{9}\Sigma\frac{1}{r^2} + \ldots\ldots\ldots\right\}, \\ &\ldots\ldots\ldots\ldots \\ R^{[n]}_n &= \frac{n^{2n+1}}{2n+1}, \end{aligned} \quad (12)$$

we have the result:

$$K_{2n,i} = G_{2n,i}\left[\frac{1}{i^2}R'_n + \frac{1}{i^4}R''_n + \frac{1}{i^6}R'''_n + \ldots + \frac{1}{i^{2n}}R^{[n]}_n\right] \quad (13)$$

The G's are functions of n and i, the R's are functions of n alone.

5. **Computations.** In order to facilitate the interpretation of formula (13) for increasing values of n the following computations for $n = 1, 2, 3$ are appended.

	$G_{2n,1}$	$G_{2n,2}$	$G_{2n,3}$
$n=1$	$(-1)^2\frac{1!\,0!}{2!\,0!}=\frac{1}{2}$		
$n=2$	$(-1)^2\frac{2!\,1!}{3!\,1!}=\frac{1}{3}$	$(-1)^3\frac{2!\,1!}{4!\,0!}=-\frac{1}{12}$	
$n=3$	$(-1)^2\frac{3!\,2!}{4!\,2!}=\frac{1}{4}$	$(-1)^3\frac{3!\,2!}{5!\,1!}=-\frac{1}{10}$	$(-1)^4\frac{3!\,2!}{6!\,0!}=\frac{1}{60}$

	R_n'	R_n''
$n=1$	$\frac{1^3}{3}=\frac{2}{6}$	
$n=2$	$\frac{2^3}{3}-\frac{2^5}{5}\left\{\frac{1}{1^2}+\frac{1}{2^2}\right\}=-\frac{480}{90}$	$\frac{2^5}{5}=\frac{576}{90}$
$n=3$	$\frac{3^3}{3}-\frac{3^5}{5}\sum_1^3\frac{1}{1^2}+\frac{3^7}{7}\sum_1^3\frac{1}{1^2 2^2}=\frac{54{,}054}{840}$	$\frac{3^5}{5}-\frac{3^7}{7}\sum_1^3\frac{1}{1^2}=-\frac{316{,}386}{840}$

	R_n'''
$n=3$	$\frac{3^7}{7}=\frac{262{,}440}{840}$.

	$K_{2n,1}$	$K_{2n,2}$
$n=1$	$G_{2,1}R_1'=\frac{1}{6}$	
$n=2$	$G_{4,1}\left[R_2'+R_2''\right]=\frac{32}{90}$	$G_{4,2}\left[\frac{R_2'}{4}+\frac{R_2''}{16}\right]=\frac{7}{90}$ [6]
$n=3$	$G_{6,1}\left[R_3'+R_3''+R_3'''\right]=\frac{27}{840}$	$G_{6,2}\left[\frac{R_3'}{4}+\frac{R_3''}{16}+\frac{R_3'''}{64}\right]=\frac{216}{840}$

	$K_{2n,3}$
$n=3$	$G_{6,3}\left[\frac{R'_3}{9}+\frac{R_3''}{81}+\frac{R_3'''}{729}\right]=\frac{41}{840}$

[6] Several mathematical and engineering handbooks have this value erroneously, $\frac{7}{80}$.

These values for the $K's$ give us well-known Cotes' formulas:

$$\int_a^b P^{[2]}(x)dx = (b-a)\left(\frac{1}{6}y_{-1} + \frac{4}{6}y_o + \frac{1}{6}y_1\right), \tag{14}$$

$$\int_a^b P^{[4]}(x)dx = (b-a)\left(\frac{7}{90}y_{-2} + \frac{32}{90}y_{-1} + \frac{12}{90}y_o + \frac{32}{90}y_1 + \frac{7}{90}y_2\right), \tag{15}$$

$$\int_a^b P^{[6]}(x)dx = (b-a)\left(\frac{41}{840}y_{-3} + \frac{216}{840}y_{-2} + \frac{27}{840}y_{-1} + \frac{272}{840}y_o + \frac{27}{840}y_1 + \frac{216}{840}y_2 + \frac{41}{840}y_3\right), \tag{16}$$

more familiar in the form,

$$\int_a^b P^{[2]}(x)dx = \frac{h}{3}(y_{-1} + 4y_o + y_1), \tag{17}$$

$$\int_a^b P^{[4]}(x)dx = \frac{2h}{45}(7y_{-2} + 32y_{-1} + 12y_o + 32y_1 + 7y_2), \tag{18}$$

$$\int_a^b P^{[6]}(x)dx = \frac{h}{140}(41y_{-3} + 216y_{-2} + 27y_{-1} + 272y_o + 27y_1 + 216y_2 + 41y_3), \tag{19}$$

where h represents the interval at which the ordinates, y_i, are spaced.

If formula (17) is applied three times successively to cover the six intervals involved in formula (19), there results

$$\int_a^b P^{[6]}(x)dx = (\text{approximately})\frac{h}{3}(y_{-3} + 4y_{-2} + 2y_{-1} + 4y_o + 2y_1 + 4y_2 + y_3). \tag{20}$$

The right-hand side of equation (20) is Simpson's Rule. It is suggestive to observe that this rule, which, when applied to $2n+1$ values of the integrand of a transcendental integral, is equivalent to the use of $2n$ parabolas to approximate the integrand, may give a closer approximation than the integral of the polynomial of degree $2n$ determined by these same $2n+1$ values.

For example, as an approximation to the transcendental integral,

$$\pi = 4\int_0^1 \frac{dx}{1+x^2}\,dx,$$

from values (rational) of the integrand for $x = 0, \frac{1}{6}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, \frac{5}{6}, 1$,

formula (19) yields 3.14157+, while formula (20) yields 3.14159+.

The study of Cotes' coefficients for increasing n is therefore of theoretical rather than practical (from the point of view of approximate integration) interest. It seems to offer a profitable field for further investigation in its bearing on the general subject of polynomial approximations.

A CERTAIN TYPE OF PRODUCT AND THE COMBINATORY ANALYSIS INVOLVED IN ITS EXPANSION[1]

By LEPINE HALL RICE

1. If from a polynomial we form a second polynomial either by deleting one or more terms or by simply repeating the first polynomial, and from the second polynomial form a third, and so on, until there are m polynomials, then it is an interesting question to ask what is the numerical coefficient of the general term in the product of these m polynomials.

The product being written

$$P=(a_1+\ldots+a_n)(a_{p_2}+\ldots+a_n)\ldots(a_{p_m}+\ldots+a_n),\ p_{i+1}\geqq p_i$$

and the general term

$$A\cdot a_{\gamma_1}^{\beta_1}a_{\gamma_2}^{\beta_2}\ldots a_{\gamma_k}^{\beta_k},\ \begin{cases}\gamma_1<\gamma_2<\ldots<\gamma_k,\\ \beta_1+\beta_2+\ldots+\beta_k=m,\end{cases}$$

let us denote by α_1 the number of polynomials (and they will be the first α_1 polynomials) which contain a_{γ_1}, and in general by α_i the number of polynomials which contain a_{γ_i}.

Having arranged the matter in this way, we find no difficulty in computing the value of A. For, let β_1 a_{γ_1}'s be first chosen from β_1 of the first α_1 polynomials. This can be done in $\binom{\alpha_1}{\beta_1}$ ways. Next let β_2 a_{γ_2}'s be chosen from the $\alpha_2-\beta_1$ polynomials remaining available among the first α_2 polynomials; this can be done in $\binom{\alpha_2-\beta_1}{\beta_2}$ ways. Then, β_3 a_{γ_3}'s can be chosen in $\binom{\alpha_3-\beta_2-\beta_1}{\beta_3}$ ways. Thus proceeding, we come finally to the β_k a_{γ_k}'s; but there is now no choice, for they must come from the β_k polynomials still remaining available. Thus we clearly have

$$A=\binom{\alpha_1}{\beta_1}\binom{\alpha_2-\beta_1}{\beta_2}\binom{\alpha_3-\beta_2-\beta_1}{\beta_3}\ldots\binom{\alpha_{k-1}-\beta_{k-2}-\ldots-\beta_1}{\beta_{k-1}}.$$

[1]Presented to the American Mathematical Society, February 26, 1921, and October 29, 1921.

2. In 1770, William Emerson[2] published a method of finding the number of combinations "with limited repetition," as we now say: that is, the number of r-combinations of a stock of different objects some or all of which may be repeated in the same combination, but not every one of which may be repeated so as to occur as many as r times. In the course of this determination, Emerson employed a procedure essentially like the foregoing, although for a different purpose. And for a still different purpose, L. Oettinger, in 1850,[3] availed himself of the same line of attack. It seems to us desirable to formulate this method in general terms, ready for use in dealing with other outwardly dissimilar cases. We begin by stating briefly, first Emerson's solution, and then Oettinger's problem and his solution. The same letters as above will be employed but with a different specific signification.

(*a*) Emerson separated the r-combinations into sets, the general set containing all those combinations in which β_1 different objects each occur exactly γ_1 times, β_2 different objects each exactly γ_2 times, and so on, up to β_k different objects which each occur exactly γ_k times. If we take $\gamma_1 > \gamma_2 > \ldots > \gamma_k$, and if α_i $(i = 1, 2, \ldots, k)$ denote the number of different objects in the stock which can be used at least γ_i times in a combination, then the number of combinations in the general set will be

$$E_g = \binom{\alpha_1}{\beta_1}\binom{\alpha_2-\beta_1}{\beta_2}\binom{\alpha_3-\beta_2-\beta_1}{\beta_3}\cdots\binom{\alpha_k-\beta_{k-1}-\ldots-\beta_1}{\beta_k}.$$

Here our present interest in Emerson's work ceases, as he simply goes on to find E_g for every possible set.

(*b*) Oettinger desired the number of r-combinations with repetitions under the restriction that if an object were chosen at all it must be used in the combination *at least* a specified number of times, while each object might be used as many as r times. He separated the r-combinations into sets, the general set containing all those combinations in which β_i different objects occur exactly γ_i times each. Taking $\gamma_1 < \gamma_2 < \ldots < \gamma_k$, and denoting by α_i the number of different objects in the stock which may, when taken, be taken as few as γ_i times, then in the general set the

[2] William Emerson, The Doctrine of Combinations, Permutations, and Compositions, of Quantities. London, 1770.

[3] L. Oettinger, Arch. f. Math., 15 (1850), p. 246, Sec. 6.

number of combinations, O_g, will be expressed in precisely the same form as E_g, above. The rest of Oettinger's summation is like that of Emerson, and does not concern us here.

3. In each case the following characteristics appear:

(1) There is a class of available entities, in which class there are k subclasses, each included in the next, the k^{th} subclass being the class itself. There are α_i entities in the i^{th} subclass.

(2) There is to be formed a set of derived entities which shall fall into k mutually exclusive subdivisions. There are to be β_i entities in the i^{th} subdivision.

(3) The β_i derived entities in the i^{th} subdivision are to be in correspondence with (as, by being identical with) β_i of the α_i entities in the i^{th} subclass; and each of the $\Sigma\beta$ derived entities is to be in correspondence with a different available entity.

(4) It is desired to find the total number of sets of derived entities which can be thus formed.

4. When once a problem has been thrown into the foregoing form, the solution is plain: The desired number is

$$\binom{\alpha_1}{\beta_1}\binom{\alpha_2-\beta_1}{\beta_2}\binom{\alpha_3-\beta_2-\beta_1}{\beta_3}\binom{\alpha_k-\beta_{k-1}-\ldots-\beta_1}{\beta_k}.$$

The difficulty may come in recognizing that we have this type of problem before us, especially since the available entities may not be used, in every case, directly as derived entities. Thus in the first case in this paper the available entities are the polynomials; the derived entities are the a's which appear in the general term and each is in correspondence with one of the available entities, *i.e.*, is drawn from one of the polynomials; the i^{th} subclass is composed of the α_i polynomials which contain $a_{\gamma i}$; the i^{th} subdivision is composed of β_i $a_{\gamma i}$'s. In Emerson's case the available entities are the different objects in the stock; the derived entities are also different objects of the stock taken into the combination; the i^{th} subclass is composed of the α_i objects which can be used as many as γ_i times; the i^{th} subdivision is composed of β_i objects each used just γ_i times. In Oettinger's case the point of view is very nearly the same as in Emerson's and hardly needs to be stated in detail.

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THE CONSTANT VOLUME GAS THERMOMETER

By Frederick G. Keyes

The greater part of the investigations which has been carried out to establish the absolute scale of temperature has resulted in the development of the technique of the constant volume thermometer rather than of the constant pressure type of instrument. The investigations resolve themselves into those made to determine the freezing or boiling points of suitable substances above the melting point of ice, and those below the latter fixed point. In both cases, special instrumental difficulties arise which are peculiar to each extreme of temperature. For example, the choice of thermometric gas at high temperature must be such that dissociation or chemical interaction of the gas in the walls of the container and adsorptive effects are obviated or minimized. At low temperatures, a field at the present time hardly touched, the choice of a container bulb is a matter of supreme importance on account of the aggravated effects which may be encountered due to adsorption. The importance of adsorption phenomena in gas thermometry has, as far as known, not been discussed, but it is evident that the effects may be far from negligible at low temperatures. Thus Langmuir[1] found at pressures as low as 0.1 mm. and at ordinary temperatures, glass and mica adsorbed inappreciable amounts of O_2, N_2, H_2, CO, CO_2 and Ar. At liquid air temperatures, however, 1 per cent to 10 per cent of the surfaces became covered with a monomolecular layer, the surfaces becoming finally saturated at higher pressures. Platinum exhibited a striking behavior, for at pressures below 0.001 mm. the surface adsorbed H_2, CO and O_2 to form a complete layer, and, moreover, the gases so adsorbed could not be driven off at 360°.

In the light of these facts platinum would be especially unsuitable for a low temperature gas thermometer container. Glass

[1] Langmuir, Jour. Am. Chem. Soc., 39, 1904-1917.

thermometer bulbs of 100 cc. capacity are usually employed for low temperature measurements, and in the case of H_2 a monomolecular layer would mean about 0.01 cc. adsorbed at liquid air temperatures. Since the bulb holds 100 cc. at 0° and one atmosphere pressure, one part in ten thousand of the gas would disappear upon cooling. Now a monomolecular layer was observed at about 0.1 mm. pressure, and at 250 mm., the pressure at liquid air temperature in a constant volume H_2 thermometer whose ice-point pressure was one atmosphere, several layers might be adsorbed. One part in 3300, corresponding to an adsorption of three layers, would change the O_2 boiling point by more than 0.05°. Hydrogen is a gas feebly adsorbed compared to N_2 or Ar, for example. Helium, however, which shows the least tendency to adsorption is, of course, the most suitable gas for low temperature gas thermometry. In the case of a gas such as N_2, adsorptive saturation at 250 mm. pressure would be likely to involve very many layers, although otherwise this gas at the boiling point of oxygen is suitable to use in the gas thermometer, since at −183° and 250 mm. pressure it is about 21° higher in temperature than corresponds to its saturation temperature.

While the question of adsorption has not been brought into the discussion of the reduction of the readings of the gas thermometer, its importance is great in connection with a problem closely related to the thermometric one. This problem concerns the measurement of the physical properties of actual gases employed as thermometric gases. In particular, the measurement of the pressure-volume-temperature relations may be given a misleading trend, which, if taken for the real property of the substance under measurements, may lead to conclusions regarding the reduction of the readings of the gas thermometer which are far from the truth. Twelve years ago, for example, a large number of observations were made by the writer on the isothermals of ammonia contained in a steel vessel. A subsequent study of the data led to the conviction that ammonia in the gas phase exhibited in its pressure-volume-temperature relations a behavior radically different from the behavior of N_2, air, O_2, or CO_2. Subsequent measurements made in such a manner as to largely swamp out the adsorptive effect of the ammonia on the container walls have shown

that ammonia in the gas phase is sensibly similar as regards its pressure-volume-temperature relations to the other substances mentioned. It is clear, therefore, that measurements involving the properties of substances at comparatively small densities may be much disturbed by the adsorptive effect, and this increasingly at lower temperatures.

During the past ten years there has been published the proof of the accuracy of an equation of state [2], [3], [4] rationally deduced. In its particular form for a gas composed of an invariable species of molecule the equation is:

$$p = \frac{RT}{v - \beta e^{-\alpha/v}} - \frac{A}{(v+l)^2}, \qquad (1)$$

and has been shown to represent accurately the pressure-volume-temperature relations of substances over wide ranges of temperature and pressure, as well as to give the derived quantities, such as the Joule-Thomson effect[5] and constant pressure specific heat to 200 atmospheres, in agreement with experiment in the case of air, in particular.

It will be noted that equation (1) is of such a form that the pressure is a linear function of the temperature at constant volume; the significance of which is that the temperatures on the constant volume gas scale must lie directly on the absolute scale. For the constant pressure scale, however, corrections are necessary, and the method of deducing the corrections will be given in a later part of the present paper. The statement regarding the linearity of pressure increase assumes, of course, that adsorption, and association or dissociation of the thermometric gas are excluded.

The methods employed hitherto to compute the corrections needed for the gas scale may be divided into two classes; first, those which depend on correlating the existing Joule-Thomson data as a function of the temperature and extrapolating by means of an empirical function to temperatures outside the limits of the actual Joule-Thomson measurements; and second, those

[2] Keyes, Proc. Nat. Acad. Sci., 3, 323, 1917.
[3] Phillips, Jour. of Math. and Phys., 1, 42, 1921.
[4] Phillips, Proc. Nat. Acad. Sci., 7, 172, 1921.
[5] Keyes, Jour. Amer. Chem. Soc., 43, 1452, 1921.

which attempt to calculate the gas scale corrections by means of an equation of state. The first method may be considered satisfactory provided the Joule-Thomson data involve no constant sources of error or trend such as would lead to an empirical function unsuitable for extrapolation. The second, or equation of state, method suffers from the defect that, should the equation of state be purely empirical and of the incorrect form, entirely erroneous conclusions may be reached regarding the whole trend of the scale corrections to the gas thermometers.

Now the proposition expressed by the equation (1) is simple and definite: the pressure of a substance, within the range of temperature and volume where association and dissociation are excluded, is asserted to be a linear function of the temperature when the volume is held constant. This proposition can be judged true or false only on the basis of experience, keeping in view that effects due to adsorption or association must be eliminated. The examination of all the available literature, the results of which have been in part published, shows that for very considerable ranges of pressure, volume and temperature the pressure increases linearly with temperature, and that, moreover, when deviations occur they are adequately accounted for on the assumption of association of the type, for example, of $N_2O_4 \rightarrow 2NO_2$ and acetic acid vapor. The possibility of association for such substances as gaseous N_2, H_2 or O_2, for example, to double molecules of the type $(N_2)_2$ as a consequence of the feebler valence forces than those described as primary valences has, so far as known, never been considered. That association exists generally, there can be no doubt, and it is easily recognized in the regions of the critical volume and temperature, or in the case of N_2 gas at ordinary temperatures at pressures above 1000 atmospheres. It has been shown, however, that Ar, N_2, O_2, air, H_2 and He, above their critical temperature, show a linear increase of pressure with temperature at constant volume up to pressures in the case of N_2, O_2, air, H_2 to 1000 atmospheres, and in the case of Ar and He over the extent of the pressure range measured, which is under 100 atmospheres. If this is true it is at once clear that at the low pressures employed in gas thermometry, the pressure must be very exactly a linear function of temperature at constant volume. Moreover, a test of

this proposition is possible. Comparisons may be made of the computed properties with the observations at low pressures; the constant volume and constant pressure mean coefficients of expansions, as well as the quantity $\left(\frac{\partial pv}{\partial p}\right)_T$, for example. Since these computations have been made with the constants of the equations which describe the high pressure behavior, agreement of the calculations with the low pressure data is evidence that linearity of pressure increase with temperature must be very exactly true at the low pressures.

It being established that, for molecules of invariable type, the pressure increases linearly with temperature at constant volume, it is of interest to investigate the effect of association as affecting the readings of the constant volume gas thermometer, since it is only by association or dissociation that the constant volume scale could fail to read on the absolute scale, it being emphasized that adsorption effects have been eliminated or allowed for separately. A possible method of detecting the latter effect in gas thermometry at constant volume would consist in observing the same fixed point at a variety of fillings of the gas thermometer, at different ice-point pressures. It can be shown that deviations from the absolute scale would vary linearly with the ice-point pressure, whereas if adsorption enters, the deviations will increase rapidly with pressure increase.

The Change of the Pressure Volume Product with Change in Pressures at Low Pressures.

There are comparatively few data relating to the change of pv with pressure at different temperatures. Professor Guye has published a considerable quantity of the observations made at the Geneva laboratory, but for the greater part these are at the temperature of melting ice only. Chappuis, however, has made measurements up to and including 100° which, with the data of several other observers, have served as a point of departure in the study of the scale corrections for the gas scale of temperature.

Equation (1) is sufficiently exact at low pressures if the constants a and l are neglected. There is obtained then, for the pv derivative with pressure, assuming that $pv = RT$ for the correction term:

$$pv = RT\frac{v}{v-\beta} - \frac{A}{v};$$

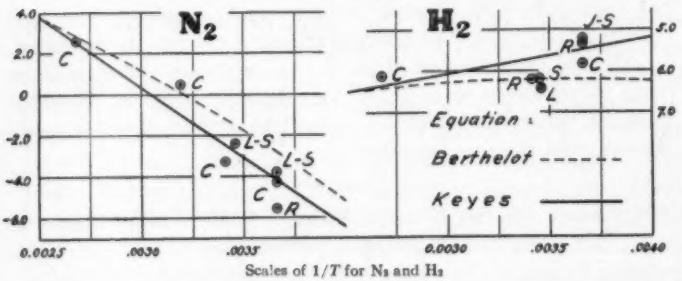
$$pv = RT + (\beta RT - A)\frac{1}{v} = RT + \left(\beta - \frac{A}{RT}\right)p;$$

$$\left(\frac{\partial pv}{\partial p}\right)_T = \beta - \frac{A}{RT}. \qquad (2)$$

The equation (2) is in reality the tangent to the pv, p curve at infinitely low pressures, but should hold with considerable exactness to pressures of one or two atmospheres.

FIG. 1. Values of $10^4 \frac{1}{p_0 v_0}\left(\frac{\partial pv}{\partial p}\right)_T$ for Nitrogen and Hydrogen Shown as a Function of $1/T$

C = Chappuis, R = Rayleigh, L-S = Leduc & Sacerdot, L = Leduc, S = Schalkwijk, J-S = Jaquerod & Scheurer

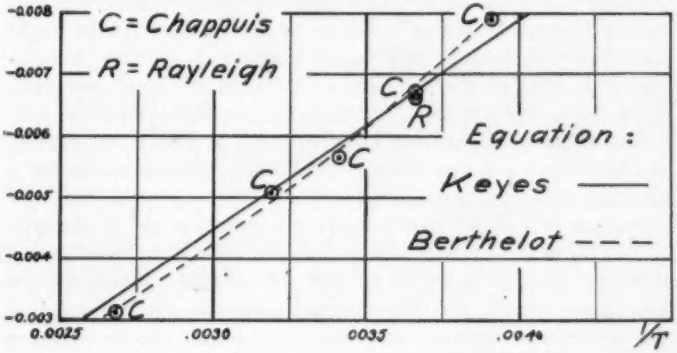


Scales of $1/T$ for N_2 and H_2

It is to be observed that the coefficient is an inverse function of the absolute temperature, and the available experimental data have been plotted with the inverse temperature in Figs. (1) and (2) for hydrogen, nitrogen and carbon dioxide. In the diagram, the dotted line represents the line drawn from Berthelot's equation which he used to obtain corrections for the gas scales. It is evident from the figure that the dotted line does not conform to the requirements of the data as well as the straight line, except in

the case of carbon dioxide. Even in this case, if the lowest temperature $(1/T=.0039, t=-17.5c)$ datum is rejected, a straight line is all that the data warrant. With carbon dioxide the adsorption effect is to be guarded against, and the low temperature point appears to be too low, as in fact it would be if adsorption disturbed the observations. As a matter of fact the trend of all the points is such as to indicate increasing adsorptive effect with falling temperature.

FIG. 2. Values of $\frac{1}{p_0 v_0}\left(\frac{\partial pv}{\partial p}\right)_T$ for Carbon Dioxide Shown as a Function of $1/T$



It is, of course, at once evident that since a van der Waal's form of equation for a gas implies no correction to the constant volume scale, the most general procedure would be to assume a correction existed, and set up as Berthelot has done, an empirical equation which makes the isometrics' curved lines. The equation of Berthelot has a form similar to that of Clausius, as follows:

$$p=\frac{RT}{v-b}-\frac{a}{v^2T}.$$

This equation gives for $\left(\frac{\partial pv}{\partial p}\right)_T$ the equation $\left[\frac{\partial pv}{\partial p}\right]_T=b-\frac{a}{RT^2}$ and to evaluate the constants it is necessary to plot the values of the coefficient against $\frac{1}{T^2}$. Figs. (1) and (2) by no means indi-

cate that greater linearity would be obtained if the coefficients were plotted against $\frac{1}{T^2}$ except in the case of carbon dioxide where possibly the observations are disturbed by adsorption. Carbon dioxide has, however, never been seriously considered as a suitable thermometric gas. In the case of N_2 and H_2 it is clear that $\left(\frac{\partial pv}{\partial p}\right)_T$ is linear in $\frac{1}{T}$.

If the true form of the equation of state for a gas consisting of molecules of invariable species is of the form (1) there is only one manner by which the readings of the constant volume gas thermometer could fail to lie on the absolute temperature scale, and that is through a change in the molecular species. There might conceivably be present appreciable numbers, in the case of nitrogen, of species of the type $[N_2]_2$ or double nitrogen molecules, or at the higher temperatures the nitrogen might dissociate into atoms, affecting the thermometer readings. A method of treating and allowing for the presence of these other types of molecules is herewith attempted as follows:

Assume first that a monoatomic or polyatomic gas of the type of He, N_2 or H_2 contains a small fraction of double molecules of the type $(He)_2$ $[N_2]_2$ or $[H_2]_2$. Let the heat of reaction for the association be ΔH, then the thermodynamic equation connecting the equilibrium constant with the temperature for the reaction $N_2 \rightleftarrows \frac{1}{2}[N_2]_2$, where x is the fraction of N_2 molecules associated, is:

$$\underline{\overline{K}} = \frac{C_{[N_2]_2}^{\frac{1}{2}}}{C_{N_2}} = \frac{\sqrt{\frac{x}{2}\left(1-\frac{x}{2}\right)}}{1-x} = M\left(e^{\frac{+\Delta H}{RT}}\right)\left(\frac{R}{v}\right)^{\frac{1}{2}} \qquad (3)$$

$$\underline{\overline{K}} = \sqrt{\frac{x}{2}} \text{ for small values of } x.$$

In this equation v is the volume of the gas at equilibrium at any temperature T; R is the gas constant per mol, and M, a constant to be determined from a knowledge of $\underline{\overline{K}}$ at any definite temperature and volume. The equation of state may be written for large volumes:

$$p = \frac{R\left(1-\frac{x}{2}\right)}{v-\beta} - \frac{A}{v^2}. \qquad (4)$$

For the constant volume thermometer the natural thermodynamic equation to be used is:

$$\left(\frac{\partial U}{\partial v}\right)_T = \lambda = T\left(\frac{\partial p}{\partial T}\right)_v - p = T^2\left(\frac{\partial \frac{p}{T}}{\partial T}\right)_v. \tag{5}$$

From (3) and (4) there are obtained for $\left(\frac{\partial p}{\partial T}\right)_v$ and λ the equations

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-\beta}\left(1-\frac{x}{2}\right) - \frac{RT}{2(v-\beta)}\left(\frac{\partial x}{\partial T}\right)_v$$

$$= \frac{R}{v-\beta}\left(1-\frac{x}{2}\right) + x\,\frac{R}{(v-\beta)}\,\frac{\Delta H}{RT}$$

$$\lambda = \frac{RT}{v-\beta}\left(1-\frac{x}{2}\right) + x\,\frac{R}{v-\beta}\,\frac{\Delta H}{R} - p$$

$$\lambda = \left(\frac{A}{v^2}\right) + \frac{R^2}{v(v-\beta)}\,m^2 e^{\frac{+2\Delta H}{RT}}\,\frac{2\Delta H}{R} \tag{6}$$

In the latter equation $\frac{A}{v^2}$ is constant in any given apparatus filling of the thermometric gas and the thermodynamic equation for the gas thermometer becomes, on integrating (5) with respect to T, setting $\frac{A}{v^2}$ equal to ϕ:

$$\frac{p}{T} - \frac{p_o}{T_o} = \phi\,\frac{T_1 - T_o}{T_o T_1} - \left(\frac{R}{v}\right)^2 m^2\left[e^{\frac{+2\Delta H}{RT}}\right]_{T_o}^{T} \cdots \tag{7}$$

The defined fixed points of melting ice and boiling water together with the pressure coefficient,

$$\frac{p_{100} - p_o}{100 p_o} = \epsilon_v,$$

give for T_o, the melting point of ice on the absolute scale, from (7), the equation:

$$T_o = \frac{1 + \frac{\phi}{p}}{C_v + \frac{T_{100}}{100 p_o} J_o^{100}} \tag{8}$$

The ice point temperature has been calculated assuming that J, the last term of equation (7), is zero and the mean value 273.13 ± 0.01 obtained from about thirty data[6] on various gases in agreement with the value arrived at empirically by Buckingham from the available Joule-Thomson data. Assuming J zero is equivalent to assuming no association. It appears clear, therefore, that as far as the data on coefficients are concerned they do not disclose an influence due to association which is appreciable. Indeed, the order of agreement in the coefficient of expansion is at best about 1 part in 10,000 as judged by the agreement between different observers, and this accuracy corresponds to about 0.03° in the temperature of the ice point.

The mode of treatment for dissociation into atoms is exactly analogous to what has been developed for association. Corrections could be computed for the constant volume scale from equation (7), were data not entirely lacking.

It is interesting to compute by means of equation (1) the corrections for the constant pressure scales of N_2, He, H_2, for comparison with the corrections based on the empirical treatment of Joule-Thomson data. The curves are calculated by the use of equation (1), from which the following equation results for the constant pressure thermometer; where t_a is the absolute centigrade scale and t, the constant pressure gas scale in question. β and A, the constants of the equation, are given in Table I.

$$t_a - t = \left[\left(\frac{\beta}{RT_o} + \frac{\Delta\epsilon}{\epsilon}\right) - \frac{A}{R^2T_o^2}\left(\frac{2+\epsilon t}{1+\epsilon t}\right)\right] p_o t \qquad (9)$$

In this equation $\Delta\epsilon$ is the difference between the actual mean volume-expansion coefficient corresponding to the ice-point pressure p_o and ϵ the reciprocal of T_o (273.13 ± 0.01). Table II gives $t_a - t$ calculated for N_2, H_2 and He, for an initial pressure of 1000 mm.

[6] Keyes, Jour. Amer. Chem. Soc., 42, 54, 1920.

TABLE I

Constants in units of volume in cubic centimeters per gram, pressure in atmospheres per square centimeter, temperature $=(273.13+t)$.

Gas	R	β	A
He	20.53	3.17	3,285
H_2	40.72	9.62	39,102
N_2	2.914	1.66	1,587
CO_2	1.865	2.912	3,219

TABLE II

Constant pressure gas scale corrections for initial pressure of 1000 mm.

t	(t_q-t)	(t_a-t)	(t_a-t)
	He	H_2	N_2
−250	0.373	1.130	
−200	0.081	0.249	2.006
−100	0.012	0.035	0.281
−50			0.082
50	−0.0008	−0.0024	−0.019
200			0.102
500			0.625
1000			1.71

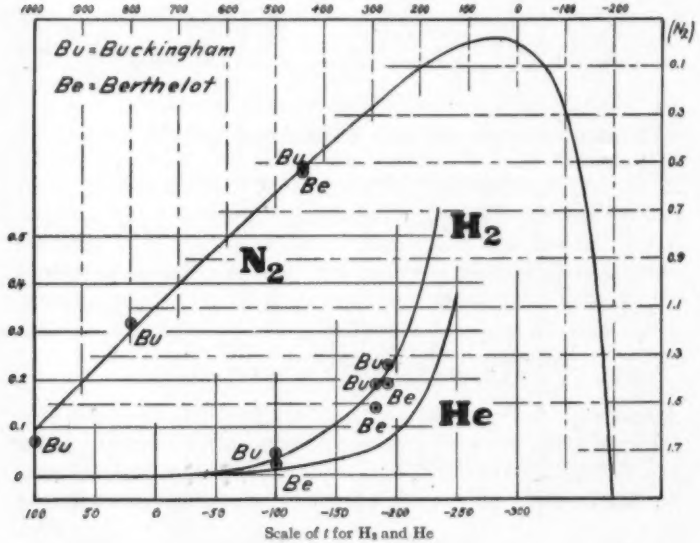
The numerical equations are as follows for 1000 mm. ice-point pressure:

$$(t_a - t)_{He} = \left[2.35 - 1.358\,\frac{2+\epsilon t}{1+\epsilon t}\right] \times 10^{-4} \times t.$$

$$(t_a - t)_{H_2} = \left[7.19 - 4.152\,\frac{2+\epsilon t}{1+\epsilon t}\right] \times 10^{-4} \times t.$$

$$(t_a - t)_{N_2} = \left[57.3 - 33.1\,\frac{2+\epsilon t}{1+\epsilon t}\right] \times 10^{-4} \times t.$$

FIG. 3. Values of Constant-pressure Thermometer Corrections, $(t_a - t)$, for N_2, H_2, He Thermometers, Shown as a Function of t Pressure at ice-point, 1000 mm.



The values in Table II are plotted in Fig. 3 with the values for the respective constant pressure scales computed by Buckingham from a corresponding-states-treatment of the Joule-Thomson data and Berthelot from his equation of state. It is notable that Buckingham's values agree very well in the case of nitrogen with

the values based on the equation (1). The agreement of the hydrogen values are also as good as can be expected in view of the meager Joule-Thomson data. Berthelot's numbers, on the other hand, are low. The Joule-Thomson data, it should be noted, can be used directly for the constant pressure scale corrections, whereas for the constant volume corrections an indirect use of the Joule-Thomson data has to be resorted to.

It has been shown that the experimental data do not indicate that a correction to the constant volume scale is required, at least at temperatures in the range -200 to 0 in the case of hydrogen and helium, and from -100 to 1000 possibly in the case of nitrogen.

SUMMARY

1. Attention has been called to the fact that adsorption on the walls of the container bulb of a gas thermometer may lead to serious error. The measurements of the coefficient

$$\left(\frac{\partial pv}{\partial p}\right)_T$$

made at different temperatures to determine the form of the equation of state for low pressures may be misleading unless adsorption effects are eliminated.

For N_2 and H_2 the coefficient is linear in the reciprocal absolute temperature which indicates that the pressure is a linear function of the absolute temperature. The coefficient for CO_2, plotted against $\frac{1}{T}$, shows some curvature, but in the direction which would be caused by adsorption.

2. It is pointed out that if adsorption as a source of error is eliminated, corrections for the constant volume scale could only arise from association or dissociation of the molecules comprising the thermometric gas. The equation is developed for this circumstance, and it is shown that the present expansion coefficients between melting ice and boiling water for the thermometric gases are given within the limits of accuracy by means of the several equations of state whose constants have been evaluated at high pressures, where the pressures are linear functions of the absolute temperature. The conclusion is drawn, therefore, that the mo-

lecular association term in the formula deduced for the temperature of melting ice on the absolute temperature scale must exert an effect less than 1 part in 10,000, which is the limit of accuracy of the present expansion coefficients.

3. Corrections are calculated for the constant pressure scale for H_2, He and N_2, on the basis of the equation of state giving the pressure as a linear function of the temperature. The N_2 and H_2 corrections agree well with those of Buckingham obtained from Joule-Thomson measurements. Berthelot's corrections are too low in the case of H_2.

THE EQUIVALENCE OF EXPANSIONS IN TERMS OF ORTHOGONAL FUNCTIONS[1]

By J. L. WALSH, OF HARVARD UNIVERSITY, AND N. WIENER.

Introduction. Suppose we are considering the nth partial sum of the formal expansion of an arbitrary function $f(x)$ in terms of the set of functions $\{\phi_n(x)\}$ normal and orthogonal on the interval $0 \leqq x \leqq 1$. This sum is

$$\sum_{i=1}^{n} \phi_i(x) \int_0^1 f(y)\phi_i(y)dy = \int_0^1 f(y) \left\{ \sum_{i=1}^{n} \phi_i(x)\phi_i(y) \right\} dy. \qquad (1)$$

If we are considering the nth partial sum of the expansion of $f(x)$ in terms of the functions $\phi_n(x)$ which together with the functions $\psi_n(x)$ form a biorthogonal set normalized over the interval (0,1), we find that this sum is

$$\sum_{i=1}^{n} \phi_i(x) \int_0^1 f(y)\psi_i(y)dy = \int_0^1 f(y) \left\{ \sum_{i=1}^{n} \phi_i(x)\psi_i(y) \right\} dy. \qquad (2)$$

If we replace the partial sums (1) and (2) by the analogous Cesàro sums of order 1, we get

$$\int_0^1 f(y) \left\{ \sum_{i=1}^{n} \frac{n-i+1}{n} \phi_i(x)\phi_i(y) \right\} dy \qquad (3)$$

$$\text{and} \int_0^1 f(y) \left\{ \sum_{i=1}^{n} \frac{n-i+1}{n} \phi_i(x)\psi_i(y) \right\} dy,$$

respectively. Similar expressions may easily be obtained for Cesàro sums of higher orders. Again, the Fourier integral representation for $f(x)$ is

$$\lim_{n\to\infty} \frac{1}{\pi} \int_{-\infty}^{\infty} f(y) \frac{\sin n(y-x)}{y-x} dy. \qquad (4)$$

All of the expressions (1) – (4) have at their nth stage, as their

[1] Presented to the American Mathematical Society, December 28, 1921

nth approximation to the arbitrary function $f(x)$, an expression of the form

$$\int_a^b f(y)\, K_n(x,y)dy. \tag{5}$$

In the expansions which have been mentioned, this represents $f(x)$ in some sense or other, either by convergence (as $n\to\infty$), or convergence in the mean, or perhaps purely formally. For certain well-known sequences $\{K_n(x,y)\}$ the nature of this mode of representation has been ascertained with more or less completeness. The question naturally arises whether for other sequences $\{K_n\}$ the problem of the mode of representation of f may not be reducible to that of better-known sequences $\{K_n\}$. This is the chief problem attacked in the present paper; the principal result is stated in Theorem I. We shall consider also the representation of a function by a given sequence $\{K_n\}$ at different points of the interval considered; the results found are stated in Theorems II and III.

It is clear that the formal expansions of a function $f(x)$ in terms of the two sequences $\{K_n\}$ and $\{K'_n\}$ will have the same properties in all that concerns convergence, convergence in the mean, uniform convergence, Gibbs's Phenomenon, etc., if merely

$$\lim_{n\to\infty}\int_a^b f(y)\left\{K_n(x,y)-K'_n(x,y)\right\}dy=0 \tag{6}$$

uniformly in x. If this is true we shall say that the formal expansions of $f(x)$ *have the same convergence properties* or are *equivalent*. If this is true for all functions $f(x)$ of summable square[2] we shall say that not only the expansions of $f(x)$ are equivalent but that the two sequences $\{K_n\}$ and $\{K'_n\}$ are equivalent. These definitions presuppose a range of values for x which is frequently $a\leqq x\leqq b$ and will be considered to be this entire interval unless otherwise specified. The range may be specified, however, as any sub-set of points on this interval.

[2] Here and throughout this paper, when we postulate the summability of the square of a function we tacitly assume that the function is measurable; it follows that the function itself is also summable.

The notion of equivalence has been employed by Haar[3] and by Young[4] in specific cases. A similar notion involving the absoluteness of the convergence of the series

$$\sum \int_a^b f(y) \left\{ K_{n+1}(x,y) - K^1_{n+1}(x,y) - K_n(x,y) + K^1_n(x,y) \right\} dy, \quad (7)$$

has been discussed in some detail by Walsh,[5] and sufficient conditions have been found for its applicability. To the knowledge of the authors, however, no necessary and sufficient conditions for equivalence have been found. The first part of the present paper is devoted to a proof of **Theorem I**, which can be expressed in a simplified form as follows:

A necessary and sufficient condition that the sequences $\{ K_n \}$ *and* $\{ K^1_n \}$ *be equivalent is that*

(a) *the expansions of all functions of a closed set*[6] *in terms of* K_n *and* K^1_n *have the same convergence properties and that*

(b) *there exist a finite* A *such that for all* n *and* x

$$\int_a^b \left\{ K_n(x,y) - K^1_n(x,y) \right\}^2 dy < A. \quad (8)$$

Haar, in the second article cited, makes use of the sufficiency of this condition in the particular case of the equivalence of the Fourier and Legendre developments, and in a footnote mentions a mode of proving its sufficiency that is of perfectly general application, employing Hilbert's theory of bilinear forms in infinitely many variables.

Theorem I is applied in the first part of the present paper to the demonstration of the equivalence of the sine and cosine series.

[3] Mathematische Annalen, Vol. 69 (1910), pp. 331–371; Vol. 78 (1917–1918), pp. 121–136. The former of these papers refers to the equivalence of the Sturm-Liouville and Fourier cosine developments, the latter refers to the equivalence of the Legendre polynomial and Fourier cosine developments.

[4] Proceedings of the London Mathematical Society, (2) Vol. XVIII, pp. 141–162, 163–200, especially pp. 156, 150. These papers consider the equivalence of the Legendre polynomial and Bessel developments to the better-known Fourier developments.

[5] Transactions of the American Mathematical Society, Vol. 22 (1921), pp. 230–239. See also a forthcoming paper in the Annals of Mathematics.

[6] A set of functions is said to be *closed* or *complete* if each function of the set is of summable square and if there is no non-null function of summable square orthogonal to every function of the set.

In the second part of this paper we discuss certain problems of the interval equivalence of expansions. Thus the Fourier sine development of an arbitrary function has in the interior of a period the following important properties:

(*a*) The convergence of the development of $f(x)$ for $x=x_1$ and the nature of the approach of the approximating functions (the partial sums) to the limit function in the neighborhood of x_1 depend merely on the values of $f(x)$ for arguments in the neighborhood of x_1;

(*b*) The nature of the approach of the approximating functions to the limit function in the neighborhood of x_1 depends in no way on the actual position of x_1 in the entire interval; in other words, the difference between the sine series for $f(x)$ in the neighborhood of x_1 and the sine series for $f(x+h)$ in the neighborhood of x_1-h converges uniformly to zero in x and h.

In order to make these properties more tangible, we formulate the following definitions:

(*a*) the sequence $\{K_n\}$ is said to be *regular* if, whenever $f(x) \equiv g(x)$ over the interval (c,d) $[a<c<d<b]$, we have

$$\lim_{n\to\infty} \int_a^b [f(y)-g(y)]\, K_n(x,y)dy = 0 \tag{9}$$

uniformly over any closed interval entirely interior to (c,d);

(*b*) the sequence $\{K_n\}$ is said to be *uniform* if it is regular and if whenever x and $x+h$ lie in the interval $(a+\epsilon, b-\epsilon)$, where ϵ is an arbitrary positive quantity, we have

$$\lim_{n\to\infty} \int_{x-\epsilon}^{x+\epsilon} f(y)\{K_n(x,y)-K_n(x+h,y+h)\}\, dy=0 \tag{10}$$

uniformly in x and h for every $f(y)$ of summable square; this is the condition already referred to, but it will be convenient to require also that

$$\lim_{n\to\infty} \int_a^b \left\{ g(x)-\int_a^b K_n(x,y)g(y)dy \right\}^2 dx=0 \tag{11}$$

shall be significant and valid for every $g(x)$ of summable square.

That condition (11) is equivalent to property (*b*) follows from

Theorem II. *If the sequence* $\{K_n\}$ *is regular, then for every* ϕ *of summable square*

$$\lim_{n\to\infty}\int_a^{x-\epsilon}\phi(y)\,K_n(x,y)dy=\lim_{n\to\infty}\int_{x+\epsilon}^{b}\phi(y)\,K_n(x,y)dy=0 \qquad (12)$$

uniformly in x *over the interval* $(a+\epsilon,\ b-\epsilon)$.

We shall prove that if $\{K_n\}$ is uniform, it is equivalent over $(a+\epsilon,\ b-\epsilon)$ to a sequence of the form $K_n(y-x)$. From this there will follow

Theorem III. *If the sequence* $\{K_n\}$ *is uniform and if* $F(x)$ *can be written in the form,*

$$\int_a^x \Phi(u)du, \qquad (13)$$

where $\Phi(u)$ *is of summable square in* (a,b), *then the formal expansion of* $F(x)$ *in terms of the sequence* $\{K_n\}$ *converges uniformly over* $(a+\epsilon,\ b-\epsilon)$ *to the value* $F(x)$.

I. **The equivalence of expansions.**

Let $\{f_n(x)\}$ and $\{\phi_n(x)\}$ be two closed sets of functions, normal and orthogonal, on the interval $0\leqq x\leqq 1$. A condition that the sequences $\{K_n\}$ corresponding be equivalent is that the sequence of functions

$$\sum_{j=1}^{n}\{f_j(x)f_j(y)-\phi_j(x)\phi_j(y)\}=Q_n(x,y) \qquad (14)$$

be equivalent to zero. If this is true we shall say that the sets $\{f_n\}$ and $\{\phi_n\}$ are equivalent; the condition for this equivalence thus reduces to the condition that for every $F(x)$ of summable square we have

$$\lim_{n\to\infty}\int_0^1 F(y)Q_n(x,y)dy=0 \qquad (15)$$

uniformly in x.

We shall now prove

Theorem I. *A necessary and sufficient condition that a sequence of functions* $\{Q_n(x,y)\}$ *of summable square in* y *should have the*

property that for every F of summable square (15) *should hold uniformly in x over a point set S contained in* (0.1) *is that there exist a number A such that for all n and for all x in S,*

$$\int_0^1 [Q_n(x,y)]^2 dy < A, \tag{16}$$

and that for all the functions $\{\psi_m\}$ of a set closed on (0, 1),

$$\lim_{n\to\infty} \int_0^1 \psi_m(y) Q_n(x,y)dy = 0 \tag{17}$$

uniformly in x over S.

The sufficiency of (16) and (17) is readily demonstrated.[7] Let $\{\psi_m\}$ be taken, as it may without essential restriction, as a closed normal orthogonal set. Then by the Riesz-Fischer theorem, a necessary and sufficient condition that a function $F(x)$ be of summable square is that we may write

$$F(x) \sim \sum_{j=1}^{\infty} a_j \psi_j(x),\ a_j = \int_0^1 F(x)\psi_j(x)dx, \tag{18}$$

where the symbol $\sim$ is to be interpreted as convergence in the mean. Moreover, by the Riesz-Fischer theory,[8] we have

$$\int_0^1 F(y)Q_n(x,y)dy = \sum_{j=1}^{\infty} a_j \int_0^1 \psi_j(y)Q_n(x,y)dy$$

$$= \sum_{j=1}^{m} a_j \int_0^1 \psi_j(y)Q_n(x,y)dy + \sum_{j=m+1}^{\infty} a_j \int_0^1 \psi_j(y)Q_n(x,y)dy. \tag{19}$$

Then we have from the general inequality,

$$\sum_{j=1}^{k} \alpha_j\beta_j \leq \left\{ \sum_{j=1}^{k} \alpha_j^2 \sum_{j=1}^{k} \beta_j^2 \right\}^{\frac{1}{2}} \tag{20}$$

which holds whatever may be the quantities α_j and β_j, we have

[7] Cf. Hilbert, Integralgleichungen, p. 148.
[8] This follows immediately from the Schwarz inequality.

$$\left| \sum_{j=m+1}^{\infty} a_j \int_0^1 \psi_j(y) Q_n(x,y)\,dy \right|$$

$$\leqq \left\{ \sum_{i=m+1}^{\infty} a_j^2 \sum_{j=m+1}^{\infty} \left[\int_0^1 \psi_j(y) Q_n(x,y)\,dy \right]^2 \right\}^{\frac{1}{2}}$$

$$\leqq \left\{ \sum_{j=m+1}^{\infty} a_j^2 \sum_{j=1}^{\infty} \left[\int_0^1 \psi_j(y) Q_n(x,y)\,dy \right]^2 \right\}^{\frac{1}{2}} \tag{21}$$

$$\leqq \left\{ \sum_{j=m+1}^{\infty} a_j^2 \int_0^1 \left[Q_n(x,y) \right]^2 dy \right\}^{\frac{1}{2}} \leqq \left\{ \sum_{j=m+1}^{\infty} a_j^2 \right\}^{\frac{1}{2}} A^{\frac{1}{2}}.$$

Let the function $F(x)$ be given. We may choose m so that the last term in (21) is less than $\epsilon/2$, by the convergence of Σa_j^2. We choose N, so that for $n > N$, $1 \leqq j \leqq m$ we have

$$\left| a_j \sum_{i=1}^{m} a_i^2 \int_0^1 \psi_j(y) Q_n(x,y)\,dy \right| \leqq \frac{\epsilon a_j^2}{2}, \tag{22}$$

for all x in S. Then it follows from (19) that

$$\left| \int_0^1 F(y)\, Q_n(x,y)\,dy \right| < \epsilon \tag{23}$$

uniformly for all x in S. This completes the proof of the sufficiency of (16) and (17).

It remains to prove the necessity of (16) and (17); in fact, merely the necessity of (16), for that of (17) is obvious. Suppose (16) not to be true. Then there are two infinite sequences of numbers n_k and x_k, such that

$$\int_0^1 \left[Q_{n_k}(x_k,y) \right]^2 dy > 2^{2k}. \tag{24}$$

Set $C_1(y) = Q_{n_1}(x_1,y)$. Let $C_2(y)$ be the first $Q_{n_k}(x_k,y)$, such that

$$\left| \int_0^1 C_2(y)\, Q_{n_1}(x,y)\, dy \right| < 1 \tag{25}$$

for all x in S; such a $Q_{n_k}(x_k,y)$ will exist because of (15). Similarly, let $C_k(y)$ be the first $Q_{n_k}(x_k,y)$, such that we have

$$\left| \int_0^1 C_k(y)\, C_j(y)\, dy \right| < 1 \tag{26}$$

for all x in S and for every $j < k$.

We now consider the series

$$\sum_{n=1}^{\infty} \frac{C_n(y)}{2^n \left\{ \int_0^1 [C_n(y)]^2 dy \right\}^{\frac{1}{2}}}, \tag{27}$$

and shall prove that this series converges in the mean. That is, we are to prove

$$\lim_{n \to \infty} \int_0^1 \left\{ \sum_{j=n}^{n+p} \frac{C_j(y)}{2^j \left\{ \int_0^1 [C_j(y)]^2 dy \right\}^{\frac{1}{2}}} \right\}^2 dy = 0; \tag{28}$$

or, what is the same thing,

$$\lim_{n \to \infty} \sum_{k=n}^{n+p} \sum_{j=n}^{n+p} \frac{\int_0^1 C_j(y)\, C_k(y)\, dy}{2^{j+k} \left\{ \int_0^1 [C_j(y)]^2 dy \int_0^1 [C_k(y)]^2 dy \right\}^{\frac{1}{2}}} = 0. \tag{29}$$

We find at once from the Schwarz inequality that

$$\int_0^1 C_j(y)\, C_k(y) dy \leqq \left\{ \int_0^1 [C_j(y)]^2 dy \int_0^1 [C_k(y)]^2 dy \right\}^{\frac{1}{2}}, \tag{30}$$

so that (29) will follow if merely

$$\lim_{n \to \infty} \sum_{k=n}^{\infty} \sum_{j=n}^{\infty} 2^{-(j+k)} = 0. \tag{31}$$

This is, however, immediately true, since

$$\sum_{k=n}^{\infty} \sum_{j=n}^{\infty} 2^{-(j+k)} = \left\{ \sum_{j=n}^{\infty} 2^{-j} \right\}^2 = 2^{2-2n}. \tag{32}$$

Hence, there is a function $\Phi(x)$ to which the series (27) converges in the mean.[9] The limit function $\Phi(x)$ is summable and of summable square, and (27) can be integrated term by term.

Let us now consider $\int_0^1 \Phi(x) C_n(x) dx$.

We have

$$\int_0^1 \Phi(x) C_n(x) dx = \sum_{m=1}^{\infty} \frac{\int_0^1 C_n(x)\, C_m(x) dx}{2^m \left\{ \int_0^1 [C_m(x)]^2 dx \right\}^{\frac{1}{2}}}. \tag{33}$$

[9] See, for example, Plancherel, Rendiconti di Palermo, Vol. 30 (1910), p. 292.

We find from (24)

$$\frac{\int_0^1 [C_n(x)]^2 dx}{2^n \left\{ \int_0^1 [C_n(x)]^2 dx \right\}^{\frac{1}{2}}} > 1; \tag{34}$$

and we find from (24) and (26)

$$\frac{\left| \int_0^1 C_n(x)\, C_m(x) dx \right|}{2^m \left\{ \int_0^1 [C_m(x)]^2 dx \right\}^{\frac{1}{2}}} < 2^{-2m}. \tag{35}$$

Then we have finally,

$$\int_0^1 \Phi(x) C_n(x) dx > 1 - \sum_{m=1}^{\infty} 2^{-2m} = \frac{2}{3}, \tag{36}$$

which is inconsistent with (15). This completes the proof of the necessity of (16) and the proof of Theorem I.

In particular, we have proved that a necessary and sufficient condition that the normal orthogonal sets $\{f_n\}$ and $\{\phi_n\}$ be equivalent is that [in the notation of (14)]

$$\int_0^1 [Q_n(x,y)]^2 dy < A \tag{37}$$

for all n and for all x on the interval (0, 1), while [$\{f_n\}$ being assumed closed]

$$\lim_{n \to \infty} \int_0^1 f_j(y)\, Q_n(x,y) dy = 0 \tag{38}$$

for every j uniformly in x.

Formulæ (37) and (38) are susceptible of a good deal of transformation. We may substitute for (37)

$$\sum_{j=1}^{n} [f_j(x)]^2 + \sum_{j=1}^{n} [\phi_j(x)]^2 - 2 \sum_{j=1}^{n} \sum_{k=1}^{n} f_j(x) \phi_k(x) \int_0^1 f_j(y) \phi_k(y) dy < A, \tag{39}$$

and for (38)

$$\lim_{n \to \infty} \left\{ f_j(x) - \sum_{k=1}^{n} \phi_k(x) \int_0^1 \phi_k(y) f_j(y) dy \right\} = 0, \tag{40}$$

uniformly in x for every j. Formula (40) simply states that the ϕ series for each f_j converges uniformly to the value f_j.

Equivalence as defined for these sets $\{f_n\}$ and $\{\phi_n\}$ refers to the identity of the convergence properties of the two series formed as in (18) from the two sets of functions. This equivalence includes equivalence of the two new series found by summing those two former series by the Cesàro mean of the first order. There is, however, an equivalence for the new series without any reference to the old series, or, what is the same thing, which involves the identity of the convergence properties of the original series so far as concerns summability or uniform summability of the first or of higher orders. The definition of this equivalence is that for every function F of summable square we must have

$$\lim_{n\to\infty}\frac{1}{n}\int_0^1 F(y)\sum_{j=1}^{n}Q_j(x,y)dy=0 \tag{41}$$

uniformly in x. For this equivalence it is necessary and sufficient that there be an A such that for all n and x

$$A>\frac{1}{n^2}\int_0^1\left\{\sum_{j=1}^{n}Q_j(x,y)\right\}^2dy=\frac{1}{n^2}\int_0^1\left\{\sum_{j=1}^{n}(n+1-j)[f_j(x)f_j(y)-\phi_j(x)\phi_j(y)]\right\}^2dy$$

$$=\frac{1}{n^2}\left\{\sum_{j=1}^{n}(n+1-j)^2\left\{[f_j(x)]^2+[\phi_j(x)]^2\right\}\right. \tag{42}$$

$$\left.-2\sum_{j=1}^{n}\sum_{k=1}^{n}(n+1-j)(n+1-k)\left\{f_j(x)\phi_k(x)\int_0^1 f_j(y)\phi_k(y)dy\right\}\right\},$$

while

$$\lim_{n\to\infty}\frac{1}{n}\int_0^1 f_j(y)\sum_{k=1}^{n}Q_k(x,y)dy=0 \tag{43}$$

uniformly in x for all j. Condition (43) may be written

$$\lim_{n\to\infty}\left[\frac{n+1-j}{n}f_j(x)-\sum_{1}^{n}\frac{(n+1-k)\phi_k(x)\int_0^1\phi_k(y)f_j(y)dy}{n}\right]=0, \tag{44}$$

which merely asserts that every f_j is the uniform Cesàro sum of its ϕ series. It is of course assumed here that the set $\{f_j\}$ is closed.

Every type of summation has a type of equivalence appropriate to it, and every such type of equivalence admits of a treatment similar to the one just given for Cesàro summability of the first kind. We shall have a boundedness condition analogous to (42) and a set of summability conditions not unlike (44).

In many cases of equivalence of the sets $\{f_n\}$ and $\{\phi_n\}$, the two sets of functions are so related that we have, for all n and x,

$$\sum_{j=1}^{n} \left\{ f_j(x) - \phi_j(x) \right\}^2 < A. \tag{45}$$

In this case it is possible to replace (39) by an equivalent condition to the effect that,

$$\left| \sum_{j=1}^{n} \sum_{k=1}^{n} A_{jk} f_j(x) \phi_k(x) \right| < B, \tag{46}$$

where

$$A_{jk} = \int_0^1 f_j(x) \phi_k(x) dx - \delta_{jk}, \tag{47}$$

δ_{jk} being the Kronecker symbol that is zero or unity according as $j \neq k$ or $j = k$.

The special case of Theorem I, where the range S is a single point, deserves some detailed consideration. Thus we have the theorem concerning a sequence $\{Q_n\}$ of functions of summable square:

In order that for all functions $F(y)$ of summable square we have

$$\lim_{n \to \infty} \int_0^1 F(y) Q_n(y) dy = 0, \tag{48}$$

it is necessary and sufficient that (48) *be true for a closed set of F's and that there be an A such that for all n*

$$\int_0^1 [Q_n(y)]^2 dy < A. \tag{49}$$

We shall now prove the following theorem:

Let there be a sequence $\{Q_n(y)\}$ such that (49) *obtains. Then a*

necessary and sufficient condition that there exist a function $Q(y)$ such that

$$\lim_{n\to\infty}\int_0^1 F(y)Q_n(y)dy = \int_0^1 F(y)Q(y)dy \tag{50}$$

for all functions $F(y)$ of summable square is that, for all functions of a closed set $\{F_m(y)\}$,

$$\lim_{n\to\infty}\int_0^1 F_m(y)Q_n(y)dy$$

exist.

The necessity of the condition is obvious; we proceed to prove its sufficiency. We clearly have the following relation, if the closed set $\{F_m(y)\}$ is chosen (as may be done with no loss of generality) as a normal orthogonal set:

$$\sum_{m=1}^{\infty}\left\{\int_0^1 F_m(y)Q_n(y)dy\right\}^2 < A. \tag{51}$$

It therefore follows that,

$$\sum_{m=1}^{\infty}\left\{\lim_{n\to\infty}\int_0^1 F_m(y)Q_n(y)dy\right\}^2 \leqq A. \tag{52}$$

Then, by the Riesz-Fischer Theorem, there exists a function $Q(y)$ of summable square such that,

$$Q(y) \sim\sim \sum_{m=1}^{\infty} F_m(y)\left\{\lim_{n\to\infty}\int_0^1 F_m(y)Q_n(y)dy\right\}, \tag{53}$$

where the sign $\sim\sim$ has the same significance as in (18).

Then we have

$$\int_0^1 Q(y)F_m(y)dy = \lim_{n\to\infty}\int_0^1 F_m(y)Q_n(y)dy, \tag{54}$$

$$\lim_{n\to\infty}\int_0^1 F_m(y)\left\{Q_n(y)-Q(y)\right\}dy = 0. \tag{55}$$

We have also

$$\int_0^1\left\{Q_n(y)-Q(y)^2\right\}dy \leqq 2\int_0^1[Q_n(y)]^2dy + 2\int_0^1[Q(y)]^2dy < 4A, \tag{56}$$

so that as in (48) we have

$$\lim_{n\to\infty}\int_0^1 F(y)\left\{Q_n(y)-Q(y)\right\}dy=0, \tag{57}$$

and our proof is complete.

It may also be remarked that if (50) is assumed, we may prove successively (55), (54), (53), (52), (49), under the assumption that the integrals that occur in (49) all exist.

The relation between $Q_n(x)$ and $Q(x)$ in (50) is analogous to convergence in the mean, and is perhaps sufficiently important to deserve a special name. The authors suggest, as a possible verbal equivalent of (50), the statement that $\{Q_n\}$ is *quasi-convergent* to Q.

The equivalence of the sine and cosine series. The nth partial sum of the sine series for $f(x)$ over the interval $(0,\pi)$ is

$$\frac{1}{2\pi}\int_0^\pi\left\{f(y)\frac{\sin(2n+1)\frac{y-x}{2}}{\sin\frac{y-x}{2}}-f(y)\frac{\sin(2n+1)\frac{y+x}{2}}{\sin\frac{y+x}{2}}\right\}dy. \tag{58}$$

The corresponding nth partial sum of the cosine series is

$$\frac{1}{2\pi}\int_0^\pi\left\{f(y)\frac{\sin(2n+1)\frac{y-x}{2}}{\sin\frac{y-x}{2}}+f(y)\frac{\sin(2n+1)\frac{y+x}{2}}{\sin\frac{y+x}{2}}\right\}dy. \tag{59}$$

The difference between these nth partial sums is

$$\frac{1}{\pi}\int_0^\pi f(y)\frac{\sin(2n+1)\frac{x+y}{2}}{\sin\frac{y+x}{2}}dy. \tag{60}$$

Accordingly, the condition analogous to (16) is the uniform boundedness of

$$\int_0^\pi \frac{\sin^2(2n+1)\frac{y+x}{2}}{\sin^2\frac{y+x}{2}}\,dy < \int_0^\pi \csc^2\frac{y+x}{2}\,dy \tag{61}$$

$$= 2\int_{\frac{x}{2}}^{\frac{\pi+x}{2}} \csc^2 u\,du = 2\cot\frac{x}{2} - 2\cot\frac{\pi+x}{2}.$$

But the extreme right-hand member of (61) is uniformly bounded over any interval $(\epsilon,\ \pi-\epsilon)$ if $\epsilon > 0$. Furthermore, the cosine expansions of the sine functions converge uniformly over $(0, \pi)$. Hence, by Theorem I, the sine and cosine expansions of an arbitrary function (summable and of summable square) have the same convergence properties over the interval $(\epsilon,\pi-\epsilon)$.

II. Regular and uniform sequences.

Let the sequence $\{K_n\}$ be regular over the interval (0,1) according to the definition already given. This is equivalent to saying that the expansion in terms of $\{K_n\}$ of a function which is of summable square and is zero throughout an interval (a,b) [which is part of the interval (0,1)] converges uniformly to zero over any closed interval (a^1,b^1) entirely interior to (a,b). That is, if ϕ is any function of summable square, we must have

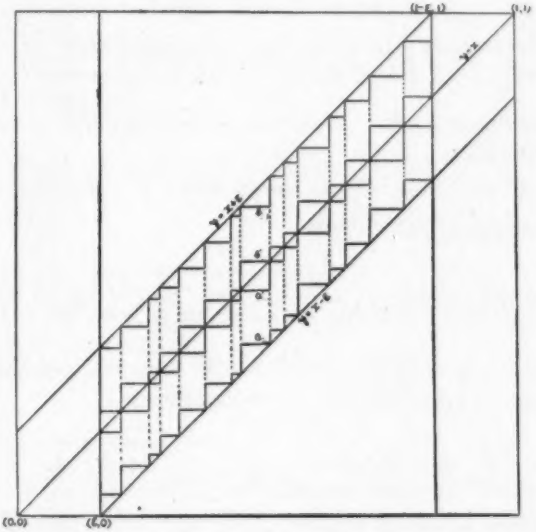
$$\lim_{n\to\infty}\int_0^a \phi(y)\,K_n(x,y)\,dy = 0,$$
$$\lim_{n\to\infty}\int_b^1 \phi(y)\,K_n(x,y)\,dy = 0, \tag{62}$$

uniformly over (a^1,b^1). It follows at once that there exists a constant A such that

$$\int_0^a [K_n(x,y)]^2\,dy < A,$$
$$\int_b^1 [K_n(x,y)]\,dy < A, \tag{63}$$

for all n and for all x in (a^1, b^1). The first of inequalities (63) must hold for every $x>a$, and the second for every $x<b$.

Consider the following diagram of the range of variation of x and y in $K_n(x,y)$:



The portion of the figure formed by the lines $x=0$, $x=\epsilon$, $x=1-\epsilon$, $x=1$, $y=0$, $y=1$, $y=x$, $y=x-\epsilon$ and $y=x+\epsilon$ needs no explanation. The parallelogram bounded by the lines $x=\epsilon$, $x=1-\epsilon$, $y=x-\epsilon$, $y=x+\epsilon$ is divided by a finite number of verticals at horizontal distances each less than $\epsilon/2$. The resulting subdivisions of this parallelogram are numbered from the left, 1, 2, . . n . . . . In the nth subdivision four horizontal lines are drawn. The line $y=b_n$ passes through the left-hand upper corner of the subdivision, that is, passes through the intersection of the left-hand bounding vertical line, and $y=x+\epsilon$. Similarly, the line $y=a_n$ passes through the right-hand lower corner, the intersection of the right-hand bounding vertical and $y=x-\epsilon$. The lines $y=a_n^1$ and $y=b_n^1$ pass through the intersection of the line $y=x$ with the left-hand and right-hand bounding verticals, respectively. Obviously we have $a_n<a_n^1<b_n^1<b_n$.

It follows immediately from (62) that we have

$$\lim_{m\to\infty}\int_0^{a_n}\phi(y)\,K_m(x,y)dy=0,$$
$$\lim_{m\to\infty}\int_{b_n}^{1}\phi(y)\,K_m(x,y)dy=0, \tag{64}$$

uniformly over (a_n^1,b_n^1). We shall use these relations to establish Theorem II.

Let us apply the Schwarz inequality to $\int_{x-\epsilon}^{a}\phi(y)\,K_m(x,y)\,dy$, where $x-\epsilon\leqq a\leqq a_n$; we have

$$\left|\int_{x-\epsilon}^{a}\phi(y)\,K_m(x,y)dy\right|\leqq\sqrt{\int_0^a\left\{K_m(x,y)\right\}^2dy\int_{x-\epsilon}^{a}\left\{\phi(y)\right\}^2dy}. \tag{65}$$

Hence, so long as $a_n^1\leqq x\leqq b_n^1$ it follows from (63) that there is a constant A_n independent of x, m and a, such that

$$\left|\int_{x-\epsilon}^{a}\phi(y)\,K_m(x,y)dy\right|\leqq\sqrt{A_n\int_{x-\epsilon}^{a}\left\{\phi(y)\right\}^2dy}. \tag{66}$$

We now subdivide each region of the x-axis between $x=a_n^1$ and $x=b_n^1$ by verticals $x=c_1^{(n)}=a_n^1$, $x=c_2^{(n)}$, . . . $x=c_p^{(n)}=b_n^1$. These lines determine a succession of triangles much like the triangles shown in the figure. Each of the new triangles is bounded by the line $y=x-\epsilon$, by a vertical line $x=c_q^{(n)}$, and by a horizontal line $y=c_{q+1}^{(n)}-\epsilon$. If we increase indefinitely the divisions in such a manner that the maximum value of $c_{q+1}^{(n)}-c_q^{(n)}$ approaches zero, and if a is always chosen so as to be the $c_{q+1}^{(n)}-\epsilon$ next greater than x, it follows from the uniform continuity of $\int_0^\xi\left\{\phi(y)\right\}^2dy$, and the fact that the A_n's are constant, that

$$\lim_{\max(c_{q+1}^{(n)}-c_q^{(n)})\to 0}\left|\int_{x-\epsilon}^{a}\phi(y)\,K_n(x,y)dy\right|=0, \tag{67}$$

uniformly for all such integrals.

Let the process of subdivision just described be carried so far that the uniform upper bound of the integrals in (67) is $\eta/2$.

It is then possible to make m so large, by (64), that

$$\left| \int_0^a \phi(y)\, K_m(x,y)dy \right| < \frac{\eta}{2}, \tag{68}$$

where the appropriate a is chosen for every x, uniformly over each of the intervals $a_n^1 \leqq x \leqq b_n^1$ and uniformly for all the intervals. Thus we have

$$\left| \int_0^{x-\epsilon} \phi(y)\, K_m(x,y)dy \right| \leqq \left| \int_0^a \phi(y)\, K_m(x,y)dy \right| + \left| \int_{x-\epsilon}^a \phi(y)\, K_m(x,y)dy \right| < \eta \tag{69}$$

uniformly for each of the intervals $a_n^1 \leqq x \leqq b_n^1$ and uniformly for all those intervals.

This means that

$$\lim_{m\to\infty} \int_0^{x-\epsilon} \phi(y)\, K_m(x,y)dy = 0 \tag{70}$$

uniformly in x for $\epsilon \leqq x \leqq 1-\epsilon$. This establishes the first part of Theorem II, and the second part may be established in precisely the same way.

Uniform expansions. If the sequence $\{ K_n \}$ is uniform over (0,1), then by Theorem II and (10) $\{ K_n \}$ is equivalent over the sub-interval $(\epsilon, 1-\epsilon)$ to the sequence whose nth term is $K_n(\epsilon, y-x+\epsilon)$ for $x-\epsilon \leqq y \leqq x+\epsilon$ and zero elsewhere. We shall denote this latter function by $K_n(y-x)$.

Then we see from (11) that

$$\lim_{n\to\infty} \int_\epsilon^{1-\epsilon} \left\{ g(x) - \int_\epsilon^{1-\epsilon} K_n(y-x)g(y)dy \right\}^2 dx = 0. \tag{71}$$

Hence, it is true uniformly for the whole class C of functions such that $\int_\epsilon^1 \{ f(x) \}^2 dx < A$, that

$$\lim_{n\to\infty} \int_\epsilon^{1-\epsilon} f(x)dx \int_\epsilon^{1-\epsilon} K_n(y-x)\, g(y)dy = \int_\epsilon^{1-\epsilon} f(x)g(x)dx. \tag{72}$$

The definition of $K_n(u)$ and (11) assure the existence of $\int_{-1}^{1} \{K_n(u)\}^2 du$. Then the Fourier series $\frac{a_0}{2} + \sum_1^\infty (a_i \cos \pi u + b_i \sin \pi u)$ of $K_n(u)$ converges in the mean to the value $K_n(u)$. Denote by $S_m(u)$ the mth partial sum of this series and by $R_m(u)$ the corresponding remainder. We clearly have

$$\int_\epsilon^{1-\epsilon} f(x)dx \int_\epsilon^{1-\epsilon} S_m(y-x)g(y)dy = \int_\epsilon^{1-\epsilon} g(y)dy \int_\epsilon^{1-\epsilon} S_m(y-x)f(x)dx,$$

for S_m is the sum of a finite number of products of functions of y by functions of x. Moreover, we have, by the Schwarz inequality,

$$\begin{aligned}
&\left[\int_\epsilon^{1-\epsilon} f(x)dx \int_\epsilon^{1-\epsilon} R_m(y-x)g(y)dy\right]^2 \\
&\leqq \int_\epsilon^{1-\epsilon} \{f(x)\}^2 dx \int_\epsilon^{1-\epsilon} \left\{\int_\epsilon^{1-\epsilon} R_m(y-x)g(y)dy\right\}^2 dx \\
&\leqq \int_\epsilon^{1-\epsilon} \{f(x)\}^2 dx \int_\epsilon^{1-\epsilon} dx \left\{\int_\epsilon^{1-\epsilon} \{R_m(y-x)\}^2 dy \int_\epsilon^{1-\epsilon} \{g(y)\}^2 dy\right\} \\
&\leqq \int_\epsilon^{1-\epsilon} \{f(x)\}^2 dx \int_{-1}^{1} \{R_m(u)\}^2 du \int_\epsilon^{1-\epsilon} \{g(y)\}^2 dy.
\end{aligned}$$

Hence, since a similar inequality holds if the integration is performed in the reverse order, we have

$$\begin{aligned}
&\int_\epsilon^{1-\epsilon} f(x)dx \int_\epsilon^{1-\epsilon} K_n(y-x)g(y)dy \\
&\qquad = \lim_{m\to\infty} \int_\epsilon^{1-\epsilon} f(x)dx \int_\epsilon^{1-\epsilon} S_m(y-x)g(y)dy \\
&\qquad = \lim_{m\to\infty} \int_\epsilon^{1-\epsilon} g(y)dy \int_\epsilon^{1-\epsilon} S_m(y-x)f(x)dx \\
&\qquad = \int_\epsilon^{1-\epsilon} g(y)dy \int_\epsilon^{1-\epsilon} K_n(y-x)f(x)dx.
\end{aligned}$$

Thus we find, from (72),

$$\lim_{n\to\infty} \int_\epsilon^{1-\epsilon} g(y)dy \int_\epsilon^{1-\epsilon} K_n(y-x)f(x)dx = \int_\epsilon^{1-\epsilon} f(x)g(x)dx. \quad (73)$$

Let us set $g(x) = 0$ outside of the interval $(2\epsilon, 1-2\epsilon)$, so that we have

$$\begin{aligned}\int_{2\epsilon}^{1-2\epsilon} f(x)g(x)dx &= \lim_{n\to\infty}\int_{2\epsilon}^{1-2\epsilon} g(y)dy\int_{\epsilon}^{1-\epsilon} K_n(y-x)f(x)dx \\ &= \lim_{n\to\infty}\int_{2\epsilon}^{1-2\epsilon} g(y)dy\int_{y-\epsilon}^{y+\epsilon} K_n(y-x)f(x)dx \\ &= \lim_{n\to\infty}\int_{2\epsilon}^{1-2\epsilon} g(y)dy\int_{-\epsilon}^{\epsilon} K_n(u)f(y-u)du \\ &= \lim_{n\to\infty}\int_{-\epsilon}^{\epsilon} K_n(u)du\int_{2\epsilon}^{1-2\epsilon} g(y)f(y-u)dy \\ &= \lim_{n\to\infty}\int_{-\epsilon+\zeta}^{\epsilon+\zeta} K_n(\eta-\zeta)d\eta\int_{2\epsilon}^{1-2\epsilon} g(y)\,f(y+\zeta-\eta)dy \\ &= \lim_{n\to\infty}\int_{0}^{1} K_n(\eta-\zeta)d\eta\int_{2\epsilon}^{1-2\epsilon} g(y)f(y+\zeta-\eta)dy,\end{aligned} \tag{74}$$

uniformly for all f's in C and for all values of ζ on the interval $(\epsilon,\ 1-\epsilon)$. Let us set $F(\eta) = f_\zeta(\zeta-\eta)$, so that we have $f_\zeta(x) = F(\zeta-x)$, and hence

$$\int_0^1\left\{ f_\zeta(x)\right\}^2 dx = \int_0^1\left\{ F(\zeta-x)\right\}^2 dx = \int_{\zeta-1}^{\zeta}\left\{ F(u)\right\}^2 du. \tag{75}$$

Then if $F(u)$ is defined over $(2\epsilon-1,\ 1-2\epsilon)$, and if $\int_{2\epsilon-1}^{1-2\epsilon}\{F(u)\}^2du$ exists, we have

$$\lim_{n\to\infty}\int_0^1 K_n(\eta-\zeta)d\eta\int_{2\epsilon}^{1-2\epsilon} F(\eta-y)g(y)dy = \int_{2\epsilon}^{1-2\epsilon} f_\zeta(x)g(x)dx \tag{76}$$

uniformly for $\epsilon \leqq \zeta \leqq 1-\epsilon$. That is, any function $\Phi(x)$ that can be expressed in the form

$$\int_{2\epsilon}^{1-2\epsilon} F(x-y)g(y)dy,$$

is the uniform limit of its expansion in terms of $\{K_n\}$.

Among the functions of the form

$$\int_{2\epsilon}^{1-2\epsilon} F(x-y)g(y)dy$$

are those for which $g(x) \equiv 1$. For such a function we have

$$\Phi(x) = \int_{2\epsilon}^{1-2\epsilon} F(x-y)dy = \int_{x+2\epsilon-1}^{x-2\epsilon} F(u)du = \int_{x+4\epsilon-1}^{x} F(\nu-2\epsilon)d\nu. \tag{77}$$

If we set $F(\nu-2\epsilon) = G(\nu)$ and let $G(\nu) = 0$ for $\nu < 0$, we find

$$\Phi(x) = \int_{0}^{x} G(\nu)d\nu \tag{78}$$

for $x \leqq 1-4\epsilon$. Thus, if we use (78) as the definition of $\Phi(x)$, the $\{K_n(x,y)\}$ expansion of Φ will converge uniformly to the value Φ over the interval $(4\epsilon, 1-4\epsilon)$. This completes the proof of Theorem III.

The property expressed in Theorem III is of course familiar in the case of the Fourier sine expansion.[10]

[10] Since receiving page proof of this paper, it has come to the attention of the authors that a necessary and sufficient condition for (48) including (49) as part of its enunciation has been given by Lebesque (*Annales de la Faculté de Toulouse*, (3), Vol. I (1909), p. 55).

AN INTEGRAL EQUATION FOR SKIN EFFECT IN PARALLEL CONDUCTORS[1]

By CHARLES MANNEBACK, Exchange Fellow, C.R.B. Educational Foundation (University of Louvain)

Consider first two infinite cylindrical non-magnetic conductors, A and B, of any cross-section, in which alternating currents of complex values I and I_1 are flowing at a frequency $f=\frac{\omega}{2\pi}$. The frequency is assumed so slow that the wave length of the oscillations is very much larger than the dimensions of the cylinders; this means that the dielectric currents need not be taken into consideration. Thus the complex current density i in the conductors will be constant along generators, and its distribution need only be investigated in a cross-section. The problem is a two-dimensional one.

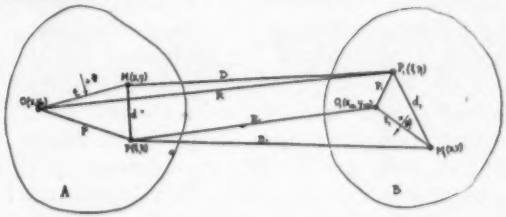


Fig 1.

We take any system of cylindrical coördinates, the z axis being parallel to the generators of the cylinders. A quantity directed along the $+z$ axis will be positive; x and y will be running coördinates, ξ and η coördinates of integration. Quantities referring to conductor A will have no indices; corresponding quantities for B will have the indices 1.

Take an arbitrary point $O(x_0,y_0)$ in A (Fig. 1). Consider any closed circuit $OMM'O'O$ in the conductor A, made up of the line OM, a parallel MM' to the $+z$ axis, another such parallel

[1]Presented to the American Mathematical Society, February 25, 1922.

OO', both of unit length and closed by the line $O'M'$. The circuit is supposed to be described in the direction $OMM'O'O$. We apply the second law of Kirchhoff to this circuit, remembering there is no current flowing along $O'M'$ and OM. The law may be stated: "Along any closed circuit, the sum of the electromotive forces and of the ohmic and inductive drops of potential is zero"; e.m.f. being taken as positive when acting in the direction followed. We have, accordingly,

$$(e-\sigma i)-(e-\sigma i_0)-\frac{d\Phi}{dt}=0, \tag{1}$$

where i and i_0 are the current densities in M and O, e the external applied e.m.f. per unit of length (which need not be known, as it cancels out), σ the resistivity of the conductor A, and Φ the total magnetic flux through the closed circuit $OMM'O'O$, all quantities being expressed in absolute units. Φ is taken as positive if it has the same direction as the flux produced by a current flowing in the circuit in the direction in which Kirchhoff's law was applied. All quantities in (1) are given their instantaneous values; everywhere else they shall be taken as complex.

The flux Φ is composed of two parts: one due to the sum (integral) of the fluxes due to all the elementary currents flowing in the conductor A, along paths parallel to the z axis. This part may be called the internal flux. The other is due to the sum (integral) of the fluxes due to all the currents external to A. This part may be called the external flux. We might assume that it is caused by currents flowing in several infinite parallel conductors, but for the sake of simplicity we shall consider only the conductor B.

The magnetic field due to a current of density i in an infinite cylindrical wire of cross-section dS is

$$\frac{2i}{l}\,.\,dS$$

at a distance l from dS. Thus the corresponding flux across the area $OMM'O'O$, due to the current density i at the point P (Fig. 1) is

$$+2i\log\frac{\rho}{d}\,dS.$$

The sum of these fluxes, extended over the conductor A, is

$$\int_A 2i(\xi,\eta)\ \log\frac{\rho}{d}\,dS(\xi,\eta),$$

where the surface integral is to be taken over the entire cross-section A, ξ and η being the variables of integration; ρ stands for the distance OP, and is a function of (ξ,η) and (x_0,y_0); d stands for the distance PM and is a function of (ξ,η) and (x,y). In the integration, (x,y) and (x_0,y_0) are constants. The integral will thus be a function of $(x,y;\ x_0,y_0)$ alone.

It is to be noticed that although ρ and d vanish during the integration the surface integral remains finite and determinate.

In a quite similar way we obtain the total external flux through $OMM'O'O$; it is

$$\int_B 2i_1(\xi,\eta)\log\frac{R}{D}\,dS(\xi,\eta),$$

where the significance of R and D is sufficiently elucidated by Fig. 1.

We consider as usual the periodic quantities associated with alternating current phenomena as the real parts of rotating plane complex vectors. We then have, formally,

$$\frac{d}{dt}=j\omega.$$

where j is symbol for $\sqrt{-1}$ and ω is 2π times the frequency. Hence, if we put

$$a=\sqrt{\frac{4\pi\omega}{\sigma}j}, \tag{2}$$

a well-known quantity occurring in every skin effect problem, the equation (1), expressing Kirchhoff's law, becomes

$$i(x,y)=i_0(x_0,y_0)+\frac{a^2}{2\pi}\int_A\log\frac{d}{\rho}i(\xi,\eta)dS(\xi,\eta)$$
$$+\frac{a^2}{2\pi}\int_B\log\frac{D}{R}i_1(\xi,\eta)dS(\xi,\eta) \tag{3}$$

The same considerations apply to the conductor B and give us the corresponding equation,

$$i_1(x,y) = i_{10}(x_{10},y_{10}) + \frac{a_1^2}{2\pi}\int_B \log\frac{d_1}{\rho_1} i_1(\xi,\eta)dS(\xi,\eta) + \frac{a_1^2}{2\pi}\int_A \log\frac{D_1}{R_1} i(\xi,\eta)dS(\xi,\eta), \qquad (3')$$

where i_{10} is the current density taken at any fixed point (x_{10},y_{10}) in the cross-section of B. The meaning of the other notations is obvious from Fig. 1.

Equations (3) and (3′) are a set of simultaneous linear integral equations of Fredholm's type, with logarithmic unsymmetrical kernels. The given functions i_0 and i_{10} are constants. The solutions $i(x,y)$, $i_1(x,y)$ will be functions of the variables (x,y) and of the constants $(x_0y_0;\ x_{10}y_{10})$ and a. Moreover they will contain the constants i_0 and i_{10}, as yet undetermined. These may be found by the two relations,

$$I = \int_A i(x,y)dS(x,y), \qquad (4)$$

$$I_1 = \int_B i_1(x,y)dS(x,y), \qquad (4')$$

where I and I_1 are the total complex currents in A and B, also known. It is possible to eliminate directly the constants i_0 and i_{10} in (3) and (3′), expressing them in terms of I and I_1, by means of (4) and (4′). This has been done for a particular case in (15).

The generalization of the set of equations (3) and (4) for any number of parallel conductors is obvious.

A special case occurs when the conductor B is so far from A that the distribution of the current in B has no longer an influence upon the distribution in A; *i.e.*, the conductor B can be replaced, as far as its action upon A is concerned, by a straight wire, carrying the total current I_1. The equations reduce to

$$i(x,y) = i_0 + \frac{a^2}{2\pi} I_1 \log\frac{D}{R} + \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho} i(\xi,\eta)dS(\xi,\eta); \qquad (5)$$

$$I = \int_A i(x,y)dS(x,y), \qquad (6)$$

where d and D are the distances MP and MB (Fig. 2), *i.e.*, functions of $(x,y;\ \xi,\eta)$ and $(x,y;\ x_{10},y_{10})$; ρ, the distance OP $(\xi,\eta;\ x_0,y_0)$; and R the constant distance OB.

The integral equation is still a Fredholm's equation, but the given function

$$i_0+\frac{a^2}{2\pi}I_1\log\frac{D}{R}$$

is no longer a constant, as it depends on (x,y).

When the wire B is so remote that the current I_1 flowing in it has no effect at all upon the distribution of the current in A, we have a further case, that of the skin effect in an isolated conductor. The equations are,

$$i(x,y)=i_0+\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}i(\xi,\eta)dS(\xi,\eta), \tag{7}$$

$$I=\int_A i(x,y)\,.\,dS(x,y), \tag{8}$$

with $d(x,y;\ \xi,\eta)$ and $\rho(x_0,y_0;\ \xi,\eta)$ defined as previously.

Skin effect in an infinite circular cylinder. If the isolated conductor A is a circular cylinder, we have a well-known problem, of which the solution is classic. We shall solve it by means of the equations (7) and (8), as an illustration and verification of the present method.

We use polar coördinates $(r,\ \Theta)$ and take the origin of the system at the point O on the axis of the cylinder. (ρ,ϕ) will be variables of integration. Noticing that the symmetrical nature of the problem calls for a solution independent of Θ, we see that the equations are,

$$i(r)=i_0+\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}i(\rho)dS(\rho,\phi), \tag{9}$$

$$I=2\pi\int_0^a i(r)rdr, \tag{10}$$

with $dS(\rho,\phi)=\rho d\rho d\phi$ as the element of area;

a, the radius of the conductor;

d, the distance PM $(x,y;\ \xi,\eta)$;

i_0, the current density at the origin, to be determined later by means of (10).

We develop a solution for $i(r)$ in (9), using Neumann's method of iteration or successive approximation. These successive values of i will be denoted by i^{I}, i^{II}, i^{III} . . . . .

Let us take a first approximation,

$$i^{\text{I}}(r)=i_0;$$

i.e., assume a current of uniform density in the cylinder. A further approximation will be obtained by substituting this value of i^{I} under the integral sign in (9); we get

$$i^{\text{II}}(r)=i_0+\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\,.\,i_0\,.\,dS(\rho,\phi);$$

or, applying (3), note 2,

$$i^{\text{II}}(r)=i_0+\frac{a^2}{2\pi}\cdot\frac{\pi r^2}{2}i_0=i_0\left[1+\left(\frac{ar}{2}\right)^2\right].$$

Substituting again, we have a third approximation,

$$i^{\text{III}}(r)=i_0+\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\,.\,i^{\text{II}}(\rho)\,.\,dS(\rho,\phi),$$

$$=i^{\text{II}}(r)+\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\,.\,i_0\left(\frac{a\rho}{2}\right)^2.\,dS(\rho,\phi),^{2}$$

$$=i^{\text{II}}(r)+i_0\left(\frac{ar}{2}\right)^4\frac{1}{(2!)^2}.$$

[2] See 4 note 2.

A fourth approximation is,

$$i^{IV}(r) = i_0 + \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\cdot i^{III}(\rho)\,.\,dS(\rho,\phi),$$

$$= i^{III}(r) + \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\cdot\frac{i_0}{(2!)^2}\left(\frac{a\rho}{2}\right)^4.\,dS(\rho,\phi),$$

$$= i^{III}(r) + i_0\left(\frac{ar}{2}\right)^6\frac{1}{(3!)^2}.$$

The k^{th} approximation is given by

$$i^k(r) = i_0 + \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\cdot i^{k-1}(\rho)\,.\,dS(\rho,\phi),$$

$$= i^{k-1}(r) + \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\cdot\frac{i_0}{[(k-1)!]^2}\left(\frac{a\rho}{2}\right)^{2k-2}.\,dS(\rho,\phi),$$

$$= i^{k-1}(r) + i_0\left(\frac{ar}{2}\right)^{2k}\frac{1}{(k!)^2}.$$

This may be developed,

$$i^k(r) = i_0\sum_{n=0}^{n=k}\frac{\left(\frac{ar}{2}\right)^{2n}}{(n!)^2},$$

with the convention that 0! means 1.

Thus *the* solution of (9) is[3]

$$i(r) = i_0\sum_{n=0}^{\infty}\frac{\left(\frac{ar}{2}\right)^{2n}}{(n!)^2}. \tag{11}$$

This power series is absolutely and uniformly convergent for all values of ar, hence is the development of an entire function.

[2] See (4), note 2.

[3] *Cf.* Goursat, Cours d'Analyse Mathematique, Vol. 3, p. 351. The fact that this series is complex makes no essential change in the proof of the unicity of the solution of a Fredholm's equation.

We recognize the development of the Bessel function of the first kind and order zero for a variable $j\alpha r$. (Note 1.)

$$i(r) = i_0 . J_0(j\alpha r). \tag{12}$$

It is easy to verify this solution by direct substitution in the integral equation (9):

$$i_0 J_0(j\alpha r) \equiv i_0 + \frac{\alpha^2}{2\pi} \int \log \frac{d}{\rho} . i_0 J_0(j\alpha\rho) . dS(\rho,\phi). \tag{13}$$

This identity is proved in note 2, equation (7).

It remains to determine the constant i_0, as yet unknown, by means of (10), expressing the known fact that the total current in the cylinder is I.

$$I = 2\pi \int_0^a i(r) r dr = 2\pi i_0 \int_0^a J_0(j\alpha r) r dr,$$

$$= 2\pi i_0 \frac{a}{j\alpha} J_1(j\alpha a).^4$$

With $S = \pi a^2$, we have,

$$i_0 = \frac{j\alpha a}{2} \frac{I}{S} \frac{1}{J_1(j\alpha a)},$$

J_1 being the Bessel function of the first kind and the first order.

The complete solution of the problem is,

$$i(r) = \frac{I}{S} \frac{j\alpha a}{2} \frac{J_0(j\alpha r)}{J_1(j\alpha a)}.^4 \tag{14}$$

The denominator never vanishes because the zeros of a Bessel function are real.

We might have eliminated i_0 between (9) and (10). If we first integrate (9) over the circle area A and then divide by $S = \pi a^2$, we obtain

[4] A. E. Kennelly, F. A. Laws and P. H. Pierce. Experimental Researches on Skin Effect in Conductors. Proc. Amer. Inst. Elect. Eng. 1915, p. 1787.

$$\frac{1}{S}\int_A i(r)dS(r,\Theta) =$$

$$\frac{1}{S}\int_A i_0 dS(r,\Theta)+\frac{a^2}{2\pi}\frac{1}{S}\int_{A_1}\int_A \log\frac{d}{\rho}\, i(\rho)dS(\rho,\phi)dS(r,\Theta).$$

If we then reverse the order of the double integration[5]

$$\frac{I}{S}=i_0+\frac{a^2}{2\pi}\int_{A_1}\left[\log\frac{a}{\rho}-\frac{1}{2}+\frac{1}{2}\left(\frac{\rho}{a}\right)^2\right]i(\rho)dS(\rho,\phi).$$

Substituting in (9),

$$i(r)=\frac{I}{S}+\frac{a^2}{2\pi}\int_A\left[\log\frac{d}{a}+\frac{1}{2}-\frac{1}{2}\left(\frac{\rho}{a}\right)^2\right]i(\rho)dS(\rho,\phi). \qquad (15)$$

This integral equation is equivalent to both (9) and (10). Its solution is thus given by (14). This result can again be verified by direct substitution.

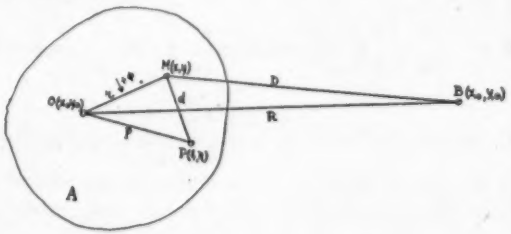


Fig 2

Eddy currents in a circular cylindrical infinite conductor, under the influence of a parallel wire. We use polar coördinates and take OB (Fig. 2′) as the initial radius for the angles Θ and ϕ. We start from (5) and (6). As (5) is linear in i, a solution will be obtained by substituting separately i_0 and $\frac{a^2}{2\pi} I_1 \log \frac{D}{R}$ under the

[5]Goursat, Vol. 3, p. 174, and (1), note (2.)

sign of integration, carrying out the method of successive approximations, in each case, and adding the results. Substituting i_0 alone we again encounter the solution $i(r)$ already obtained in (12) for the skin effect in an isolated circular cylinder. Substituting the logarithmic term alone, we shall find a solution $\iota(r,\Theta)$ that represents thus the action of the wire B upon the conductor A, *i.e.*, the eddy currents induced in A, or what might be called the proximity effect of B upon A.

We write,

$$\iota(r,\Theta)=\frac{a^2}{2\pi}I_1\log\frac{D}{R}+\frac{a^2}{2\pi}\int_A\log\frac{d}{\rho}\,\iota(\rho,\phi)dS(\rho\phi). \tag{16}$$

For every point of the cross-section A we have the uniformly and absolutely convergent series

$$\log\frac{D}{R}=-\sum_{n=1}^{\infty}\frac{1}{n}\left(\frac{r}{R}\right)^n\cos n\Theta.$$

We shall first find a solution $\iota_n(r,\Theta)$ of the integral equation

$$\iota_n(r,\Theta)=-\frac{a^2}{2\pi}I_1\frac{1}{n}\left(\frac{r}{R}\right)^n\cos n\Theta+\frac{a^2}{2\pi}\int_A\log\frac{d}{\rho}\,\iota_n(\rho,\phi)dS(\rho,\phi). \tag{17}$$

We shall see that the series $\sum_{n=1}^{\infty}\iota_n$ is absolutely and uniformly convergent for every point in A, and thus is the unique solution of (16), for the integrand in (16) may be integrated term by term.

We solve (17) by the process of successive approximations:[6]

$$\iota_n^{\mathrm{I}}(r,\Theta)=-\frac{a^2}{2\pi}I_1\frac{1}{n}\left(\frac{r}{R}\right)^n\cos n\,\Theta$$

$$\iota_n^{\mathrm{II}}(r,\Theta)=\iota_n^{\mathrm{I}}(r,\Theta)+\frac{a^2}{2\pi}\int_A\log\frac{d}{\rho}\,.\,\iota_n^{\mathrm{I}}(\rho,\phi)\,.\,dS(\rho,\phi)$$

$$=\iota_n^{\mathrm{I}}(r,\Theta)\left[1+\frac{\left(\frac{ar}{2}\right)^2}{1(n+1)}-\frac{\left(\frac{aa}{2}\right)^2}{1\,.\,n}\right]$$

[6] See (5), note 2.

$$\iota_n^{\mathrm{III}}(r,\Theta) = \iota_n^{\mathrm{I}}(r,\Theta) + \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\,.\,\iota_n^{\mathrm{II}}(\rho,\phi)\,.\,dS(\rho,\phi)$$

$$= \iota_n^{\mathrm{II}}(r,\Theta) + \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\frac{\left(\frac{a\rho}{2}\right)^2}{1(n+1)}\,\iota_n^{\mathrm{I}}(\rho,\phi)dS(\rho,\phi)$$

$$- \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\frac{\left(\frac{aa}{2}\right)^2}{1\,.\,n}\,\iota_n^{\mathrm{I}}(\rho,\phi)dS(\rho,\phi)$$

$$= \iota_n^{\mathrm{II}}(r,\Theta) + \iota_n^{\mathrm{I}}(r,\Theta)\left[\frac{\left(\frac{ar}{2}\right)^4}{1\,.\,2(n+1)(n+2)} - \frac{\left(\frac{aa}{2}\right)^2\cdot\left(\frac{ar}{2}\right)^2}{1.1.n(n+1)}\right.$$

$$\left. + \left(\frac{1}{1^2n^2} - \frac{1}{1\,.\,2\,.\,n(n+1)}\right)\left(\frac{aa}{2}\right)^4\right].$$

$$\iota_n^{\mathrm{IV}}(r,\Theta) = \iota_n^{\mathrm{I}}(r,\Theta) + \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\,\iota_n^{\mathrm{III}}(\rho,\phi)dS(\rho,\phi)$$

$$= \iota_n^{\mathrm{III}}(r,\Theta) + \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\frac{\left(\frac{a\rho}{2}\right)^4}{1\,.\,2(n+1)(n+2)}\,\iota_n^{\mathrm{I}}(\rho,\phi)dS(\rho,\phi)$$

$$- \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\frac{\left(\frac{aa}{2}\right)^2\cdot\left(\frac{a\rho}{2}\right)^2}{1\,.\,n\,.\,1(n+1)}\,\iota_n^{\mathrm{I}}(\rho,\phi)dS(\rho,\phi)$$

$$+ \frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\left(\frac{1}{1^2n^2} - \frac{1}{1\,.\,2\,.\,n(n+1)}\right)\left(\frac{aa}{2}\right)^4\iota_n^{\mathrm{I}}(\rho,\phi)\,dS(\rho,\phi)$$

$$= \iota_n^{III}(r,\Theta) + \iota_n^{I}(r,\Theta)\left[\frac{\left(\frac{ar}{2}\right)^6}{1.2.3(n+1)(n+2)(n+3)} - \frac{\left(\frac{a\alpha}{2}\right)^6}{1.2.3.n(n+1)(n+2)}\right]$$

$$- \iota_n^{I}(r,\Theta)\left[\frac{\left(\frac{ar}{2}\right)^4}{1.2(n+1)(n+2)} - \frac{\left(\frac{a\alpha}{2}\right)^4}{1.2.n(n+1)}\right]\frac{\left(\frac{a\alpha}{2}\right)^2}{1.n}$$

$$+ \iota_n^{I}(r,\Theta)\left[\frac{\left(\frac{ar}{2}\right)^2}{1.(n+1)} - \frac{\left(\frac{a\alpha}{2}\right)^2}{1.n}\right]\left(\frac{1}{1^2.n^2} - \frac{1}{1.2.n(n+1)}\right)\left(\frac{a\alpha}{2}\right)^4$$

Developing $\iota_n^{III}(r,\Theta)$, the value for $\iota^{IV}(r,\Theta)$ can be written as a product of two polynomials in $\left(\frac{ar}{2}\right)^2$ and $\left(\frac{a\alpha}{2}\right)^2$, which yields us, except for terms in a of degree higher than 6,

$$\iota_n^{IV}(r,\Theta) = \iota_n^{I}(r,\Theta)\left[1 + \frac{\left(\frac{ar}{2}\right)^2}{1(n+1)} + \frac{\left(\frac{ar}{2}\right)^4}{1.2(n+1)(n+2)} + \frac{\left(\frac{ar}{2}\right)^6}{1.2.3(n+1)(n+2)(n+3)}\right]$$

$$\times\left[1 - \frac{\left(\frac{a\alpha}{2}\right)^2}{1.n} + \left(\frac{1}{1^2.n^2} - \frac{1}{1.2.n(n+1)}\right)\left(\frac{a\alpha}{2}\right)^4 - N\left(\frac{a\alpha}{2}\right)^6\right]$$

$$\text{with } N = \frac{1}{1^3.n^3} - \frac{2}{1.2.1.n.n(n+1)} + \frac{1}{1.2.3.n(n+1)(n+2)}.$$

With a like convention, we also have[7]

[7] This transformation is suggested by the known fact that the general solution of a Fredholm's equation is a meromorphic function of the parameter a^2, and thus may be written as a quotient of two entire functions.

$$\iota_n^{IV}(r,\Theta) = \iota_n^{I}(r,\Theta)\frac{\left[1+\frac{\left(\frac{ar}{2}\right)^2}{1(n+1)}+\frac{\left(\frac{ar}{2}\right)^4}{1.2(n+1)(n+2)}+\frac{\left(\frac{ar}{2}\right)^6}{1.2.3(n+1)(n+2)(n+3)}\right]}{\left[1+\frac{\left(\frac{aa}{2}\right)^2}{1.n}+\frac{\left(\frac{aa}{2}\right)^4}{1.2n(n+1)}+\frac{\left(\frac{aa}{2}\right)^6}{1.2.3n(n+1)(n+2)}\right]}$$

or, remembering the value of $\iota_n^{I}(r,\Theta)$,

$$\iota_n^{IV}(r,\Theta) = \frac{I_1}{S}\left(\frac{a}{R}\right)^n ja a \frac{\frac{\left(\frac{jar}{2}\right)^n}{n!}\times\left[\quad\right]}{\frac{\left(\frac{jaa}{2}\right)^{n-1}}{(n-1)!}\times\left[\quad\right]},$$

where the brackets represent respectively the numerator and denominator of the fraction in the preceding expression.

In the numerator and denominator of the latter expression we recognize the four first terms of the development[8] of $J_n(ja r)$ and $J_{n-1}(jaa)$, which suggest, as the solution of (17),

$$\iota_n(r,\Theta) = \frac{I_1}{S}\left(\frac{a}{R}\right)^n ja a \frac{J_n(ja r)}{J_{n-1}(jaa)}\cos n\Theta. \tag{18}$$

As there are no adequate tables of the ratio of two Bessel's functions, it will usually be desirable for purposes of computation to employ the series development of $\iota_n(r,\Theta)$ in powers of a. It did not seem worth while to work out the general term of the approximation, because this purely heuristic solution has still to be verified. This is done in (8), note 2, where the solution (18) for ι_n leads to an identity when substituted in (17).

We now write formally, as the solution of (16),

$$\iota(r,\Theta) = \frac{I_1}{S} ja a \sum_{n=1}^{\infty}\left(\frac{a}{R}\right)^n \frac{J_n(ja r)}{J_{n-1}(jaa)}\cos n\Theta. \tag{19}$$

[8]See (1), note 1.

As this series is absolutely and uniformly convergent for every point in the cross-section A, $\iota(r,\Theta)$ is actually the solution of (16).

The denominators never vanish, since the J_n's have only real roots. We also see that (6) is identically satisfied, since

$$\int_A \iota_n \ (r,\Theta) \, . \, dS(r,\Theta) = 0.$$

This is a general property of eddy currents in parallel conductors.

To prove the uniform convergence of the series (19) we write for every point in A

$$\left| \left(\frac{a}{R}\right)^n \frac{J_n(j\alpha r)}{J_{n-1}(j\alpha a)} \cos n\Theta \right| \leq \left(\frac{a}{R}\right)^n \frac{|J_n(j\alpha r)|}{|J_{n-1}(j\alpha a)|} \leq \frac{|\alpha| a}{2} \cdot \frac{1}{n} \left[\frac{a(1+\epsilon)}{R}\right]^n$$

For, referring to the definition of J_n and J_{n-1}, note 1, we have for every point in A

$$|J_n(j\alpha r)| = \left(\frac{|\alpha| r}{2}\right)^n \frac{1}{n!}(1+\epsilon_1) \leq \left(\frac{|\alpha| a}{2}\right)^n \frac{1}{n!}(1+\epsilon_1)$$

$$|J_{n-1}(j\alpha a)| = \left(\frac{|\alpha| a}{2}\right)^{n-1} \frac{1}{(n-1)!}(1+\epsilon_2)$$

$$\text{or} \quad \frac{|J_n(j\alpha r)|}{|J_{n-1}(j\alpha a)|} \leq \frac{|\alpha| a}{2} \frac{1}{n}(1+\epsilon_3),$$

where the positive quantities ϵ may be chosen as small as we like, for every point in A, provided we have

$$n > N,$$

N being a sufficiently large fixed positive number, independent of the point considered in A.

As we always have $a < R$ it follows that $a(1+\epsilon) < R$, if ϵ is small enough. We see thus that the moduli $|\iota_n|$ in every point of A can be made less than the corresponding terms of same rank in the convergent series of constant and positive terms

$$\frac{|I_1|}{S} \frac{(|\alpha| a)^2}{2} \sum_{n=1}^{\infty} \frac{1}{n} \left[\frac{a(1+\epsilon)}{R}\right]^n.$$

This is a well-known criterion of uniform and absolute convergence.

Eddy currents in an infinite cylindrical conductor due to a uniform perpendicular alternating magnetic field. This is the case when the conductor B is so far from A that the current I_1 flowing in it produces a practically uniform magnetic field H, in phase with I_1 throughout the conductor A. (19) reduces to

$$\iota_1 = \frac{j\alpha}{2\pi} H \frac{J_1(j\alpha r)}{J_0(j\alpha a)} \cos\Theta \tag{20}$$

$$\text{with } H = \frac{2I_1}{R}.$$

at low frequencies, (20) becomes[9]

$$\iota_1 = -\frac{\alpha^2}{4\pi} H r \cos\Theta. \tag{21}$$

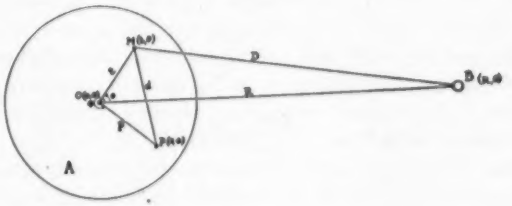


Fig 2[1]

This shows a distribution of eddy currents proportional to the induced *e.m.f.;* it means that the magnetic field of the induced currents is negligible as compared with the impressed field H. The current lags behind the impressed field in every point of A by $90°$.

At high frequencies (20) becomes[9]

$$\iota_1 = -\frac{\alpha}{2\pi} H \sqrt{\frac{a}{r}} e^{-\alpha(a-r)} \cos\Theta \tag{22}$$

This shows that the eddy currents are distributed along a given radius after the fashion of a very strongly damped wave. The current at the surface of the conductor lags behind the impressed

[9]See note 1, (6) and (7).

magnetic field by 45°. The instantaneous value of ι_1 is given at any point by multiplying the expression for ι_1 by $e^{j\omega t}$ and taking the real part of the product.

It may be demonstrated, though we shall not prove it here, that the eddy current losses in the conductor A vary at low frequency as the square of the frequency, and at high frequency as the square root of the frequency.

To summarize, we have obtained a general set of integral equations, giving the theoretical solution of the current distribution in parallel conductors[10]. Solving them by the method of successive approximations, it will naturally not be possible in every case to identify the series obtained with developments of known functions, as for example in this paper. This method, however, is interesting in giving the approximate solution of skin effect problems at low frequency for parallel conductors of any shape and number. The integrations might be performed mechanically. A physical interpretation of the successive approximations is obvious. The integral equations may also be used as a check on solutions obtained by other processes.

In these respects the method resembles the process of successive approximations used by H. B. Dwight[11] for finding the skin effect in tubular and flat conductors, although this latter method does not seem to be extended to problems in more than one variable.

Thanks are due to Dr. Wiener of the Mathematical Department of the Massachusetts Institute of Technology for reading the manuscript of this paper and also for several suggestions of detail.

[10] See note 3 and 4.
[11] Trans. Amer. Inst. Elec. Eng. Vol. 37, p. 1378, June 1918.

Note 1

The following well-known formulas of the Bessel functions are given here for convenient reference:

$$J_n(z)=\left(\frac{z}{2}\right)^n \sum_{k=0}^{\infty} \frac{\left(\frac{jz}{2}\right)^{2k}}{k!(n+k)!}, \qquad j=\sqrt{-1} \tag{1}$$

We have the relations between Bessel functions of different orders

$$J_{n-1}+J_{n+1}=\frac{2n}{z}J_n; \tag{2}$$

$$J_{n-1}-J_{n+1}=2\frac{dJ_n}{dz}; \tag{3}$$

$$\frac{dJ_0}{dz}=-J_1; \tag{3'}$$

and

$$\int z^{n+1}J_n(z)dz=z^{n+1}J_{n+1}(z); \tag{4}$$

$$\int z^{-n+1}J_n(z)dz=-z^{-n+1}J_{n-1}(z). \tag{5}$$

We also have

$$J_n(0)=0. \qquad n\neq 0.$$
$$J_0(0)=1.$$

For small values of z

$$J_n=\frac{\left(\frac{z}{2}\right)^n}{n!}+\ \ldots \tag{6}$$

For large values of z, there is an asymptotic expression,

$$j^{-n}\cdot J_n(jz)=\frac{e^z}{\sqrt{2\pi z}} \tag{7}$$

holding for z complex.[13]

[13] Jahnke und Emde, Funktionentafeln mit Formeln und Kurven. Leipzig, 1909, pp. 90, 100, 165.

Note 2

$\operatorname{Log}\frac{d}{\rho}$ admits of absolutely and uniformly convergent developments, d being the distance between the points (r,Θ) and (ρ,ϕ). We have

for $0<\rho<r$,

$$\log\frac{d}{\rho}=\log\frac{r}{\rho}-\sum_{k=1}^{\infty}\frac{1}{k}\left(\frac{\rho}{r}\right)^{k}\cos k(\phi-\Theta); \tag{1}$$

for $0\leq r<\rho$,

$$\log\frac{d}{\rho}=-\sum_{k=1}^{\infty}\frac{1}{k}\left(\frac{r}{\rho}\right)^{k}\cos k(\phi-\Theta). \tag{2}$$

Both series hold for $\rho=r$, provided $\phi\neq\Theta$. These developments may be obtained by taking the real part of the expansion of

$$\log\left[\frac{r}{\rho}e^{j(\phi-\Theta)}-1\right] \quad \text{and} \quad \log\left[1-\frac{r}{\rho}e^{j(\phi-\Theta)}\right]$$

with $j=\sqrt{-1}$.

In the integral,

$$\int_{A}\log\frac{d}{\rho}\,dS(\rho,\phi), \qquad dS(\rho,\phi)=\rho d\rho d\phi,$$

extended over the area A of a circle of radius a, whose center is at the origin, we may replace $\log\frac{d}{\rho}$ by its absolutely and uniformly convergent development and integrate term by term. All terms depending upon $(\phi-\Theta)$ vanish, and we obtain

$$\begin{aligned}\int_{A}\log\frac{d}{\rho}\,.\,dS(\rho,\phi)&=2\pi\int_{0}^{r}\log\frac{r}{\rho}\,.\,\rho\,.\,d\rho,\\&=2\pi\left[\log\frac{r}{\rho}\,.\,\frac{\rho^{2}}{2}\right]_{0}^{r}+2\pi\int_{0}^{r}\frac{1}{2}\rho d\rho,\\&=\frac{\pi r^{2}}{2}.\end{aligned} \tag{3}$$

It has already been noticed that the surface integral remains finite, although $\log \frac{d}{\rho}$ becomes infinite for $\rho = 0$.

In general, we have by the same process, k being a positive integer,

$$\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\cdot\frac{\left(\frac{a\rho}{2}\right)^{2k-2}}{[(k-1)!]^2}\cdot dS(\rho,\phi) = a^2\int_0^r \log\frac{r}{\rho}\cdot\frac{\left(\frac{a\rho}{2}\right)^{2k-2}}{[(k-1)!]^2}\cdot\rho d\rho$$

$$= \frac{\left(\frac{ar}{2}\right)^{2k}}{(k!)^2}. \tag{4}$$

We notice that the surface integral is independent of the values of the integrand in the ring ($\rho = r$, $\rho = a$). This expresses mathematically the fact that a current flowing in a cylindrical tube has no magnetic field in the interior.

In a similar way, we carry out the integration,

$$\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\,\iota_n^A(\rho,\phi)dS(\rho,\phi),$$

over the area of the circle A of radius a, where

$$\iota_n^1(\rho,\phi) = -I_1\frac{a^2}{2\pi}\frac{1}{n}\left(\frac{\rho}{R}\right)^n\cos n\phi = A_n\left(\frac{\rho}{R}\right)^n\cos n\phi.$$

All but one of the terms of the expression of $\log\frac{d}{\rho}$ will yield vanishing terms in the integral, for we have

$$\int_0^{2\pi}\cos k(\phi-\Theta)\cdot\cos n\phi\, d\phi \quad \begin{cases} = 0 & \text{for } k \neq n. \\ = \pi\cos n\Theta & \text{for } k = n. \end{cases}$$

$$\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\cdot\iota_n^1(\rho,\phi)\cdot dS(\rho,\phi)$$

$$= \frac{a^2}{2\pi}\int_0^r\int_0^{2\pi}\left[-\frac{1}{n}\left(\frac{\rho}{r}\right)^n\cos n(\phi-\Theta)\right]\left[A_n\left(\frac{\rho}{R}\right)^n\cos n\phi\right]d\phi\cdot\rho d\rho$$

$$+\frac{a^2}{2\pi}\int_r^a\int_0^{2\pi}\left[-\frac{1}{n}\left(\frac{r}{\rho}\right)^n\cos n(\phi-\Theta)\right]\left[A_n\left(\frac{\rho}{R}\right)^n\cos n\phi\right]d\phi\,.\,\rho d\rho$$

$$=-\frac{a^2}{2\pi}A_n\,.\,\frac{1}{n}\,.\,\pi\cos n\Theta\left[\int_0^r\frac{\rho^{2n}}{r^nR^n}\rho d\rho+\int_r^a\frac{r^n}{R^n}\rho d\rho\right]$$

$$=-\frac{a^2}{2\pi}A_n\,.\,\frac{1}{n}\,.\,\pi\cos n\Theta\left[\frac{r^2}{2(n+1)}+\frac{a^2-r^2}{2}\right]\left(\frac{r}{R}\right)^n$$

$$=A_n\left(\frac{r}{R}\right)^n\cos n\Theta\,.\left[\frac{\left(\frac{ar}{2}\right)^2}{n+1}-\frac{\left(\frac{aa}{2}\right)^2}{n}\right]$$

$$=\iota_n^1(r,\Theta)\left[\frac{\left(\frac{ar}{2}\right)^2}{n+1}-\frac{\left(\frac{aa}{2}\right)^2}{n}\right]. \tag{5}$$

In general we have, k being a positive integer,

$$\frac{a^2}{2\pi}\int_A\log\frac{d}{\rho}\iota_n^1(\rho,\phi)\left(\frac{a\rho}{2}\right)^{2k-2}dS(\rho,\phi)$$

$$=\iota_n^1(r,\Theta)\left[\frac{\left(\frac{ar}{2}\right)^{2k}}{k(n+k)}-\frac{\left(\frac{aa}{2}\right)^{2k}}{k\,.\,n}\right]. \tag{6}$$

As for (3), by developing $\log\frac{d}{\rho}$ in series and integrating by parts, we calculate the integral

$$\frac{a^2}{2\pi}\int_A\log\frac{d}{\rho}J_o(ja\rho)dS(\rho,\phi)=a^2\int_0^r\log\frac{r}{\rho}J_o(ja\rho)\rho d\rho$$

$$=\left[\log\frac{\rho}{r}\,.\,J_1(ja\rho)\,.\,ja\rho\right]_{\rho=0}^{\rho=r}-\int_0^r J_1(ja\rho)d(ja\rho)$$[13]

$$=J_o(jar)-1.$$

Hence we have the identity

$$i_oJ_o(jar)\equiv i_o+\frac{a^2}{2\pi}\int_A\log\frac{d}{\rho}i_oJ_o(ja\rho)dS(\rho,\phi), \tag{7}$$

that is a check on the solution (12) obtained for (9).

[13] See (3′) and (4), note 1.

As in (5), note 2, we calculate the integral

$$\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\cdot J_n(ja\rho)\cos n\phi\cdot dS(\rho,\phi)$$

$$=-\frac{a^2}{2}\cos n\theta\cdot\frac{1}{n}\cdot\left[r^{-n}\int_0^r \rho^{n+1}\cdot J_n(ja\rho)\cdot d\rho+r^n\int_r^a \rho^{-n+1}J_n(ja\rho)\cdot d\rho\right]$$

and by means of (4) and (5), note 1,

$$=-\frac{a^2}{2}\cos n\theta\cdot\frac{1}{n}\left[r^{-n}\left(\frac{\rho^{n+1}}{ja}\cdot J_{n+1}(ja\rho)\right)_{\rho=o}^{\rho=r}\right.$$

$$\left.+r^n\left(-\frac{\rho^{-n+1}}{ja}\cdot J_{n-1}(ja\rho)\right)_{\rho=r}^{\rho=a}\right]$$

$$=\frac{ja}{2}\cos n\theta\cdot\frac{1}{n}\cdot\left[r\cdot J_{n+1}(jar)+r\cdot J_{n-1}(jar)-\left(\frac{r}{a}\right)^n\cdot a\cdot J_{n-1}(ja\rho)\right].$$

using (2), note 1,

$$=\frac{ja}{2}\cos n\theta\cdot\frac{1}{n}\left[\frac{2n}{ja}J_n(jar)-\left(\frac{r}{a}\right)^n\cdot a\cdot J_{n-1}(jaa)\right]$$

$$=J_n(jar)\cdot\cos n\theta-\frac{jaa}{2}\cdot\frac{1}{n}\left(\frac{r}{a}\right)^n\cdot\cos n\theta\cdot J_{n-1}(jaa).$$

Multiplying both sides by the constant

$$\frac{I_1}{S}\left(\frac{a}{R}\right)^n jaa\cdot\frac{1}{J_{n-1}(jaa)},$$

we obtain the identity,

$$\iota_n(r,\theta)\equiv-\frac{a^2}{2\pi}I_1\frac{1}{n}\left(\frac{r}{R}\right)^n\cos n\theta+\frac{a^2}{2\pi}\int_A\log\frac{d}{\rho}\iota_n(\rho,\phi)dS(\rho,\phi), \quad (8)$$

where

$$\iota_n(r,\theta)=\frac{I_1}{S}\left(\frac{a}{R}\right)^n jaa\,\frac{J_n(jar)}{J_{n-1}(jaa)}\cos n\theta.$$

This substantiates the solution (18) of the integral equation (17).

Note 3

Equation (7) may be written

$$i-i_o=\frac{a^2}{2\pi}\int_A \log\frac{d}{\rho}\, i(\xi,\eta)dS(\xi,\eta),$$

and shows that $i-i_o$ is the difference of two logarithmic potentials whose mass density in A is equal to $\frac{a^2}{2\pi}\, i(\xi,\eta)$.

Generalizing, we have

$$i(x,y,z)=\frac{a^2}{4\pi}\int_V \frac{i(\xi,\eta,\zeta)}{r}\, dv(\xi,\eta,\zeta),$$

where r is the distance between points $(x,y,z;\ \xi,\eta,\zeta)$, V the volume of the conductor, dv the element of volume and i a space vector. This vector integral equation expresses i by means of a vector potential of mass density $\frac{a^2}{4\pi}\, i(\xi,\eta,\zeta)$. The extension to n conductors is immediate.

Note 4

Instead of considering cylindrical conductors of finite cross-section A, B . . . we may consider infinitely thin cylindrical conductors or straps.

We then have, quite as for the general case,

$$\frac{di(x)}{dx}=\frac{a^2}{2\pi}\int_{-a}^{+a}\frac{i(\xi)}{x-\xi}\, d\xi,$$

where a flat strip has been taken for sake of simplicity, extending from $x=-a$ to $x=+a$. a has the same value as before, where the volume resistivity σ has been changed into a surface resistivity. The equation is an integrodifferential one. The generalization for several non-flat straps is immediate.

Note 5

Instead of considering the current density i in the conductors, we now consider the electric field, which exists inside and outside the conductors. Inside the conductors it is equal to σi, σ being the resistivity.

We obtain for the axial component E of the field, *i.e.*, the component parallel to the generators of the cylindrical non-magnetic conductors, after a reasoning already used for obtaining the current density, this integral equation.

$$E(x,y) = E(x_0,y_0) + \frac{a^2}{2\pi}\int_S \log\frac{d}{\rho}\, E(\xi,\eta)\, dS(\xi,\eta) \qquad (1)$$

x,y are the coördinates of any point inside or outside the conductors; (x_0,y_0), the coördinates of an arbitrary fixed point. The integral is to be taken over the cross-sections of all the conductors. a is the same as before. .

Starting from the Maxwell's equations of the electromagnetic field, we find in the present case the following equations for determining E:

$$\frac{\partial^2 E_1}{\partial x^2} + \frac{\partial^2 E_1}{\partial y^2} = 0 \quad \text{outside of the conductors} \qquad (2)$$

$$\frac{\partial^2 E_2}{\partial x^2} + \frac{\partial^2 E_2}{\partial y_2} - a^2 E_2 = 0 \quad \text{inside the conductors}$$

$$\text{with } a^2 = \frac{4\pi\omega}{\sigma}\, j \qquad \text{and } i = \sqrt{-1}$$

E is logarithmic at infinity; at the boundaries between the conductors and the surrounding medium we have

$$E_1 = E_2 \qquad (3)$$

$$\frac{\partial E_1}{\partial n} = \frac{\partial E_2}{\partial n}$$

where $\partial/\partial n$ means the derivative taken along the normal to the boundary. The latter condition is equivalent in the present case

to that of the continuity of the tangential component of the magnetic field.

From this we conclude that the problem of solving the system (2) with the conditions (3) is the same as solving the integral equation (1). But in (1) the conditions at the boundary have disappeared.

NOTE ON THE NORMAL PLANES TO A SURFACE IN A SPACE OF FOUR DIMENSIONS

By C. L. E. Moore

1. **Introduction.** In this note two questions are considered. First, under what conditions will the normal planes to a surface F in a space of four dimensions envelop a second surface F'. Second, under what conditions does a surface in this space have a surface parallel to it.

The normal planes to a surface in 4-space do not, in general, have an envelope. The locus of the points of intersection of one of these planes with the nearby planes is, in general, a non-degenerate conic while the locus of the points of intersection of a tangent plane with the nearby tangent planes degenerates into two straight lines. So we have at once a necessary condition that the normal planes to a surface F envelope a surface F', *viz.*, the locus of the intersection of a given plane with the nearby planes factors into two straight lines. We shall see that this condition is also sufficient. In case this condition is identically satisfied the correspondence between F and F' is such that the characteristics on F (curves such that tangent planes at two nearby points intersect in a line) correspond to characteristics on F'.

Two parallel surfaces in 3-space have the same congruence of normals and the distances between corresponding points is constant. The second question discussed in this paper is whether it is possible to have parallel surfaces in 4-space satisfying both of these conditions, and how many. It is found that, in general, there is no surface parallel to a given surface. In case certain relations are satisfied there is a two-parameter family of surfaces having the same congruence of normal planes, but the second condition of parallelism is not satisfied. However if the surface is such that the derivative of any normal vector has no component in the normal plane then there is a two-parameter family satisfying both conditions for parallelism.

2. **The intersection of nearby planes of a congruence.** A normal plane to a surface is cut by the nearby normal planes in a conic.[1] This is true for any congruence of planes.[2]

Let the family of planes, in homogeneous coördinates, be

$$\Sigma A_i x_i = 0, \qquad \Sigma B_i x_i = 0, \qquad i = 1, 2 \ldots 5, \tag{1}$$

where A_i and B_i are functions of two parameters u, v. The point of intersection of any plane with a nearby plane is given by the solutions of the equations

$$\Sigma A_i x_i = 0, \qquad \Sigma B_i x_i = 0,$$

$$\Sigma\left(\frac{\partial A_i}{\partial u}du + \frac{\partial A_i}{\partial v}dv\right)x_i = 0,$$

$$\Sigma\left(\frac{\partial B_i}{\partial u}du + \frac{\partial B_i}{\partial v}dv\right)x_i = 0.$$

The coördinates of the point of intersection will then be a quadratic expression in $du : dv$ and consequently the locus of the point of intersection will be a conic. To determine the conditions under which the planes of (1) will be the tangent planes to a surface we will take the dual of this system of planes. By the duality the planes of the congruence will go into the two-parameter family of lines of a ruled hypersurface, the points of intersection of nearby planes will go into the 3-spaces containing two nearby lines; that is, into the tangent hyperplanes to the ruled hypersurface. If the planes of (1) envelope a surface then the hypersurface will be such that it has only a two-parameter family of tangent hyperplanes each of which is tangent at every point of one of the generators of the hypersurface.[3] If this is the case Segre showed that each line is cut by two nearby lines. By the duality two lines that cut correspond to two planes of (1) which lie in the same 3-space or which have a line in common. Hence *if the planes of* (1) *are the tangent planes of a surface it is necessary*

[1] Wilson and Moore, Differential geometry of two dimensional surfaces in hyperspace, Proc. Amer. Acad. Arts and Sciences, vol. 52, 1916, p. 326.

[2] Segre, Preliminari di una theoria delle varieatá luoghi di spazi, Rend. Circolo Math. di Palermo, vol. xxx, 1910, pp. 87–121.

[3] Segre, *loc. cit.*

and sufficient that the conic (the locus of the points in which a given plane is cut by the nearby planes) *should degenerate into a pair of straight lines.* This relation of course is to be identically satisfied.

If (1) is the congruence of normal planes to a surface then the locus of intersection of a given plane with the nearby planes will be the inverse of the pedal of the indicatrix.[4] If the normal planes envelope a surface this locus will be two straight lines. The pedal of the indicatrix will then become two circles passing through the surface point, which means that the tangents to the indicatrix will have to pass through two points and hence the indicatrix (which is always an ellipse the points of which correspond to real directions on the surface) will degenerate into a line segment. The necessary and sufficient condition that the indicatrix reduce to a line segment (not passing through the surface point) is that the characteristics (directions on the surface such that the tangent planes at two nearby points will intersect in a line) intersect at right angles. Hence *if the characteristics of a surface* F *form an orthogonal curve system on the surface, the normal planes to the surface will envelop a second surface* F′.

The correspondence between F and F' is such that the characteristics of F correspond to the characteristics of F'. For if the indicatrix of F is a line segment then the characteristics of F correspond to the ends of this segment. The tangents to the characteristics of F' will be the lines into which the locus of the intersection with nearby planes degenerates, but these two lines are seen to correspond to the ends of the indicatrix of F. If this indicatrix is AB then the characteristic corresponding to A is such that tangent planes at nearby points in this direction intersect in a line tangent to the other characteristic[5] and likewise for F'. Hence the characteristic of F corresponding to A will correspond to the characteristic of F' which corresponds to B.

If F is a developable whose indicatrix reduces to a line segment then the lines joining the ends of the indicatrix to the surface point intersect at right angles[6] and hence the characteristics of

[4] Wilson and Moore, *loc. cit.*, p. 328.

[5] Segre, Su una clarse di superficie degl' iperspazii, Atti Accad. Realle delle Scienze di Torino, 1906–7.

[6] Wilson and Moore, *loc. cit.*, p. 332.

F' will be orthogonal and consequently the normal planes of F' will also envelop a surface F''. An example of such a surface is the surface generated by rotating a logarithmic spiral in the $x_1x_3=$ plane by the rotation[7]

$$x_1'=x_1\cos t-x_2\sin t, \qquad x_2'=x_1\sin t+x_2\cos t,$$
$$x_3'=x_3\cos t-x_4\sin t, \qquad x_4'=x_3\sin t+x_4\cos t. \tag{2}$$

3. **Parallel surfaces.** In order to determine the condition for parallel surfaces we will investigate the condition that a congruence of planes have a surface normal to them; that is, the condition that the given congruence be the congruence of normal planes of a surface. Let the given congruence be represented vectorially by

$$\xi=a+bt+c\tau, \tag{3}$$

where a, b, c are vectors, functions of u, v, and t and τ are parameters. When t and τ vary while u, v are held fixed ξ, will generate the given plane of the congruence. We will assume that b and c satisfy the relations

$$b^2=c^2=1, \qquad b.c=0. \tag{4}$$

From (4) by differentiation we have

$$b.db=c.dc=0, \qquad b.dc+db.c=0. \tag{5}$$

The necessary and sufficient condition that (3) be a congruence of normal planes is that it is possible to determine t and τ as functions of u, v, so that the resulting surface has ξ for its normal plane. If this is possible then $d\xi$ will be normal to both b and c since b and c are two vectors lying in the plane of the congruence. Then

$$d\xi.b=d\xi.c=0.$$

Which, using (5), reduces to

$$b.da+dt+\tau b.dc=0,$$
$$c.da+d\tau+tc.db=0.$$

[7] C. L. E. Moore, Surfaces of rotation in a space of four dimensions, Annals of Math., vol. xxi, 1919.

Expanding in terms of du, dv, and putting in the condition that du, dv are arbitrary, we have

$$\begin{aligned} b.\frac{\partial a}{\partial u}+\tau b.\frac{\partial c}{\partial u} &= +\frac{\partial t}{\partial u}, \\ b.\frac{\partial a}{\partial v}+\tau b.\frac{\partial c}{\partial v} &= -\frac{\partial t}{\partial v}, \\ c.\frac{\partial a}{\partial u}+tc.\frac{\partial b}{\partial u} &= -\frac{\partial \tau}{\partial u}, \\ c.\frac{\partial a}{\partial v}+tc.\frac{\partial b}{\partial v} &= -\frac{\partial \tau}{\partial v}. \end{aligned} \tag{6}$$

Putting

$$b.\frac{\partial a}{\partial u}=-A,\quad b.\frac{\partial a}{\partial v}=-B,\quad c.\frac{\partial a}{\partial u}=-C,\quad c.\frac{\partial a}{\partial v}=-D,$$

$$b.\frac{\partial c}{\partial u}=-c.\frac{\partial b}{\partial u}=-P,\quad b.\frac{\partial c}{\partial v}=-c.\frac{\partial b}{\partial v}=-Q,$$

equations (6) become

$$\begin{aligned} A+P\tau &= \frac{\partial t}{\partial u}, & B+Q\tau &= \frac{\partial t}{\partial v}, \\ C-Pt &= \frac{\partial \tau}{\partial u}, & D-Qt &= \frac{\partial \tau}{\partial v}. \end{aligned} \tag{7}$$

We are then to determine the solutions of this set of equations in terms of u, v. It is obvious that this set will not be consistent unless

$$\begin{aligned} \frac{\partial}{\partial v}(A+P\tau) &= \frac{\partial}{\partial u}(B+Q\tau), \\ \frac{\partial}{\partial v}(C-Pt) &= \frac{\partial}{\partial u}(D-Qt). \end{aligned}$$

Expanding these and substituting the values of $\frac{\partial t}{\partial u}$, $\frac{\partial t}{\partial v}$, $\frac{\partial \tau}{\partial u}$, $\frac{\partial \tau}{\partial v}$,

from (7) we obtain

$$\begin{aligned} \tau\left(\frac{\partial P}{\partial v}-\frac{\partial Q}{\partial u}\right)&=\frac{\partial B}{\partial u}-\frac{\partial A}{\partial v}+QC-PD, \\ t\left(\frac{\partial P}{\partial v}-\frac{\partial Q}{\partial u}\right)&=\frac{\partial C}{\partial v}-\frac{\partial D}{\partial u}+QA-PB. \end{aligned} \tag{8}$$

The values of t and τ are therefore, in general, uniquely determined. The values of t and τ from (8) will obviously not satisfy (7) unless certain relations are satisfied by the coefficients. These relations are obtained by direct substitution in (7). A set of normal planes to a surface will satisfy these conditions, but this shows that, in general, there is no other surface having the same set of normal planes.

If

$$\frac{\partial P}{\partial v}-\frac{\partial Q}{\partial u}=0, \tag{9}$$

then t, τ cannot be determined from (8). In this case, in addition to (9), the coefficients will satisfy the relations

$$\begin{aligned} \frac{\partial B}{\partial u}-\frac{\partial A}{\partial v}+QC-PD&=0, \\ \frac{\partial C}{\partial v}-\frac{\partial D}{\partial u}+QA-PB&=0, \end{aligned} \tag{10}$$

and we have to solve (7) subject to relations (9) and (10). We can evidently make the coefficients satisfy enough relations besides these so that (7) will have a solution. Suppose this done and let t_0, τ_0 be any particular solution of (7), then the general solution can be expressed by

$$t=t_0+t_1, \qquad \tau=\tau_0+\tau_1,$$

where t_1, τ_1 satisfy the reduced system

$$\begin{aligned} \frac{\partial t_1}{\partial u}&=P\tau_1, & \frac{\partial t_1}{\partial v}&=Q\tau_1, \\ \frac{\partial \tau_1}{\partial u}&=-Pt_1, & \frac{\partial \tau_1}{\partial v}&=-Qt_1. \end{aligned} \tag{11}$$

Eliminating τ_1 from the first two,

$$Q\frac{\partial t_1}{\partial u} - P\frac{\partial t_1}{\partial v} = 0 \tag{12}$$

The solution of this last equation is an arbitrary function of the solution of

$$Pdu + Qdv = 0,$$

which from (9) is seen to be exact. Let $f(u,v)$ satisfy

$$df = Pdu + Qdv,$$

then the solution of (12) is

$$t_1 = F(f).$$

Substituting this in the first equation of (11),

$$\tau_1 = \frac{dF(f)}{df} = F'(f).$$

Putting these values in the last equation of (11)

$$F'' = -F,$$

and hence

$$t_1 = K_1 \cos (f + K_2),$$
$$\tau = -K_1 \sin (f + K_2).$$

These values satisfy (11). We can then write the general solution of (7) in the form

$$t = t_0 + K_1 \cos (f + K_2),$$
$$\tau = \tau_0 - K_1 \sin (f + K_2).$$

In this case, then, there is a two-parameter family of surfaces having the same congruence of normal planes, but obviously the distance between corresponding points is not constant and consequently the surfaces are not truly parallel.

If

$$P = Q = 0,$$

relation (10) reduces to

$$\frac{\partial B}{\partial u} - \frac{\partial A}{\partial v} = 0, \qquad \frac{\partial D}{\partial u} - \frac{\partial C}{\partial v} = 0,$$

and the solutions of the equations (7) are then the solutions of the two exact equations,

$$Adu+Bdv=dt,$$
$$Cdu+Ddv=d\tau,$$

or

$$t=t_0+K_1, \qquad \tau=\tau_0+K_2.$$

From (3) if $K_1=K_2=0$, the surface point is determined by putting in the values of t_0, τ_0. Then for values of K_1 and K_2 different from zero we see that the distance between corresponding points is

$$K_1b+K_2c,$$

and since b, c are unit vectors this is the same for all corresponding points. Hence in this case there is a two-parameter family of parallel surfaces. This is the real generalization of parallel surfaces in 3-space. An example of a surface of this kind is the surface generated by rotating a circle with center at the origin and lying in the x_1x_3-plane by the rotation (2). This is a developable surface and all the normal planes pass through O.

If (3) represents the normal planes to a surface then by the notation used by Wilson and Moore[8] $b=z$, $c=w$, and the relation $P=Q=0$ is

$$z.w_s=\nu_s=0.$$

Hence for this last case $\nu_s=0$; hence $\nu_s=0$ *is the necessary and sufficient condition that the surface be one of a two-parameter family of parallel surfaces,* or *the necessary and sufficient condition that a surface belong to a family of parallel surfaces is that the derivatives of the normals to the surface have no component in the normal plane.*

From the fact that the locus of intersection of nearby normal planes is the inverse of the pedal of the indicatrix it follows that the character of the indicatrix will be the same for all surfaces having the same congruence of normal planes. That is, if the indicatrix of one reduces to a line segment, all the others will have the same property; if the indicatrix of one passes through the surface point, so will it for all the others, etc.

[8] *Loc. cit.*, p. 304.

4. **Families of planes of $n-2$ parameters in $n-$space.** The results of the last section can readily be extended to space of n dimensions. Let the family of planes be represented vectorially by

$$\xi = a + bt + c\tau, \tag{13}$$

where a, b, c are vectors, functions of u_1, u_2 . . . u_{n-2} and b, c satisfy the relations

$$b^2 = c^2 = 1, \qquad b.c = 0.$$

The condition, then, that a variety $\mathbf{v}_{n-2}$ have these planes for normal planes is the same as before and by similar notation is

$$A_i + P_i\tau = \frac{\partial t}{\partial u_i}, \qquad i = 1, 2, \ldots n-2.$$

$$B_i - P_i t = \frac{\partial \tau}{\partial u_i}.$$

Putting in the condition for exact differentials as before, we obtain equations exactly similar to (8). Hence, in general, there is a single $\mathbf{v}_{n-2}$ normal to a *normal* family of planes. In case $\Sigma P_i du_i$ is an exact differential, there is a two-parameter family of such varieties. For, as before, the solution of the reduced system

$$\Sigma P_i\tau = \frac{\partial t}{\partial u_i}, \qquad -\Sigma P_i t = \frac{\partial \tau}{\partial u_i},$$

is

$$t = K_1 \cos(f + K_2), \qquad \tau = -K_1 \sin(f + K_2),$$

and the solution of the general set is

$$t = t_0 + K_1 \cos(f + K_2), \qquad \tau = \tau_0 - K_1 \sin(f + K_2),$$

where f satisfied $df = \Sigma P_i du_i$. The varieties in this case are not parallel, but if

$$P_i = 0$$

then there is a two-parameter family of parallel varieties having the same family of normal planes.

5. **The general case.** The condition that

$$\xi = a_i + \alpha_i t_i, \qquad i = 1, 2, \ldots K,$$

a_i, α_i being functions of $n-k$ parameters u_j, be the normal spaces to a variety $\mathbf{v}_{n-k}$, by similar notation and assumptions on α_i can be written

$$A_{ij} + \sum_k P_{kij} t_k = \frac{\partial t_i}{\partial u_j}.$$

The coefficients satisfy the following relations:

$$A_{ij} = A_{ji}, \qquad P_{iij} = 0, \qquad P_{kij} = -P_{ikj}.$$

Putting in the condition for an exact differential we are led to the statement that, in general, when ξ is a normal system there is only variety $\mathbf{v}_{n-k}$ having it for its system of normals, but that there are cases when there is an infinite system of such varieties but that these are not parallel except in the case

$$P_{kij} = 0.$$

There is an infinite set of parallel varieties $\left(\text{if } \frac{\partial A_{ik}}{\partial u_j} = \frac{\partial A_{ij}}{\partial u_k}\right)$.

COMMUTATIVITY OF CONTACT TRANSFORMATIONS OF MECHANICS

By S. D. ZELDIN

1. In this note we consider two conservative dynamical systems defined by their potential energies U_1 and U_2 (functions of the generalized coördinates) and their kinetic energies T_1 and T_2 (quadratic functions of the generalized velocity components). Moreover, we shall assume that T_1 and T_2 differ only by a factor, and that the systems are each of two degrees of freedom.

It is well known that with each of those systems there is associated an infinitesimal contact transformation whose characteristic function is of special type. In this note we shall prove that:

If two contact transformations associated with the dynamical systems described above are independent they cannot be commutative.

2. Let B_1f and B_2f, where

$$B_1f=\xi_1(x,y,p)\frac{\partial f}{\partial x}+\gamma_1(x,y,p)\frac{\partial f}{\partial y}+\pi_1(x,y,p)\frac{\partial f}{\partial p},$$

$$B_2f=\xi_2(x,y,p)\frac{\partial f}{\partial x}+\gamma_2(x,y,p)\frac{\partial f}{\partial y}+\pi_2(x,y,p)\frac{\partial f}{\partial p},$$

represent the symbols of two independent infinitesimal contact transformations, *i.e.*, $B_1f\neq cB_2f$ (c is a constant), and let their corresponding characteristic functions be $W_1(x,y,p)$ and $W_2(x,y,p)$. Then, as is known, a lineal element (x,y,p) is transformed into a neighboring element $(x+\delta x,\ y+\delta y,\ p+\delta p)$ by the transformation B_1f according to the formulas

$$\delta x=W_{1p}\delta t,\ \delta y=(pW_{1p}-W_1)\delta t,\ \delta p=-(W_{1x}+pW_{1y})\delta t,$$

and by B_2f according to the formulas

$$\delta x=W_{2p}\delta t,\ \delta y=(pW_{2p}-W_2)\delta t,\ \delta p=-(W_{2x}+pW_{2y})\delta t.$$

In order that B_1f and B_2f should be commutative (*i.e.* in order that $B_1B_2f = B_2B_1f$) we must have, as has been shown[1],)

$$\text{(a)} \qquad [W_1W_2] - W_1\frac{\partial W_2}{\partial y} + W_2\frac{\partial W_1}{\partial y} \equiv 0,$$

where

$$[W_1W_2] = \frac{\partial W_1}{\partial p}\left(\frac{\partial W_2}{\partial x} + p\frac{\partial W_2}{\partial y}\right) - \frac{\partial W_2}{\partial p}\left(\frac{\partial W_1}{\partial x} + p\frac{\partial W_1}{\partial y}\right).$$

3. Consider now the case of a particle moving in a plane. The kinetic energy is then of the form $T = \frac{1}{2}(x^2+y^2)$, and the associated characteristic functions of our two dynamical systems will be of the form

$$W_1 = \Omega_1(x,y)\sqrt{1+p^2}\ , \quad W_2 = \Omega_2(x,y)\sqrt{1+p^2}.$$

(It should be remarked here that Kasner has shown[2] that the alternant of two contact transformations of the type considered here is in general a point transformation.)

Substituting the values of W_1 and W_2 in (a) and replacing the ratios $\frac{W_1}{W_2} = \frac{\Omega_1}{\Omega_2}$ by $n(x,y)$ we get

$$p\frac{\partial n}{\partial x} - \frac{\partial n}{\partial y} \equiv 0.$$

But this equation is only satisfied when n is a constant, which means that $W_1 =$ constant $\times\ W_2$, or, what is the same thing, B_1f and B_2f are not independent. But since that is contrary to our assumption B_1f and B_2f *cannot be commutative*.

4. Consider now the general case of two degrees of freedom, which is equivalent to the motion of a particle constrained to remain on an arbitrary surface. The characteristic functions can then be written[3]

$$W_1 = \Omega_1(x,y)\sqrt{E+2Fp+Gp^2},$$

$$W_2 = \Omega_2(x,y)\sqrt{E+2Fp+Gp^2}.$$

[1] Lie-Scheffers, Berührungs-Transformationen, p. 125.
[2] Bull. Amer. Math. Soc., Vol. 16, 1910, pp. 408–412.
[3] Kasner, loc. cit., p. 410.

Denoting the ratio $\frac{W_1}{W_2}=\frac{\Omega_1}{\Omega_2}$ by $\nu(x,y)$ and substituting in (a), we get

$$p(F\nu_y-G\nu_x)-F\nu_x+E\nu_y\equiv 0,$$

where

$$\nu_x=\frac{\partial\nu}{\partial x},\quad \nu_y=\frac{\partial\nu}{\partial y}.$$

But that equation is only satisfied when ν is a constant, which again is contrary to our assumption, since, when ν is a constant, B_1f and B_2f are not independent. Therefore here again B_1f and B_2f *are not commutative.*

ON THE EXPRESSION OF THE SUM OF ANY TWO DETERMINANTS AS A DETERMINANT OF MORE DIMENSIONS

By LEPINE HALL RICE

1. The question here considered is whether the sum of any two or more determinants, of a given number of dimensions, a given signancy[1], and a given order, can be expressed as a determinant of more dimensions. The answer is that the sum can be so expressed, one more dimension being required if there are two given determinants, two more dimensions if there are four ($=2^2$) given determinants, and so on. We shall proceed from the simplest particular cases toward a general formulation of the result.

2. A permanent[2] of one dimension is a single term. Evidently the sum of any two one-dimensional or one-way permanents may be written either as a 2-way permanent or as a 2-way determinant:

$$a_1 a_2 + b_1 b_2 = \left[\begin{matrix}+\\+\end{matrix}\right| \begin{matrix} a_1 b_2 \\ b_1 a_2 \end{matrix} \Big| = \begin{vmatrix} a_1 b_2 \\ -b_1 a_2 \end{vmatrix};$$

$$a_1 a_2 a_3 + b_1 b_2 b_3 = \left[\begin{matrix}+\\+\end{matrix}\right| \begin{matrix} a_1 b_2 \cdot \\ \cdot a_2 b_3 \\ b_1 \cdot a_3 \end{matrix} \Big| = \begin{vmatrix} a_1 b_2 \cdot \\ \cdot a_2 b_3 \\ b_1 \cdot a_3 \end{vmatrix};$$

. . . . . .

$$a_1 a_2 \ldots a_n + b_1 b_2 \ldots b_n =$$

$$\left[\begin{matrix}+\\+\end{matrix}\right| \begin{matrix} a_1 & b_2 & \cdot & \ldots & \cdot & \cdot \\ \cdot & a_2 & b_3 & \ldots & \cdot & \cdot \\ \cdot & \cdot & a_3 & \ldots & \cdot & \cdot \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \cdot & \cdot & \cdot & \ldots & a_{n-1} & b_n \\ b_1 & \cdot & \cdot & \ldots & \cdot & a_n \end{matrix} \Big| = \begin{vmatrix} a_1 & b_2 & \cdot & \ldots & \cdot & \cdot \\ \cdot & a_2 & b_3 & \ldots & \cdot & \cdot \\ \cdot & \cdot & a_3 & \ldots & \cdot & \cdot \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \cdot & \cdot & \cdot & \ldots & a_{n-1} & b_n \\ (-1)^{n-1} b_1 & \cdot & \cdot & \ldots & \cdot & a_n \end{vmatrix}. \quad (1)$$

[1] The notation and the terms used in this paper are in general the same as in a paper on *P-way determinants, with an application to transvectants*, by the present writer, in *Amer. Journ. of Math.* for July, 1918, vol. xl, p. 242. The *signancy* of a determinant is its character in respect to the directions which are, and the directions which are not, regarded in fixing the signs of its terms; the former are called *signant*, the latter *nonsignant*.

[2] A *permanent* results when all the directions are made nonsignant. The present work will involve permanents as well as determinants. It will be quite evident from the notation in each case whether they are included or not.

3. There is here a clue to the form to be given to the matrix of a determinant Δ of any number of dimensions in order that it may represent the sum of any two determinants A and B, of one less dimension, A and B being of the same signancy and of the same order.[3]

Thus if A and B are determinants of two dimensions, we shall have, for the second order[4]

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} + \begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix} = \begin{vmatrix} \left[\begin{matrix}\pm\\+\\\pm\end{matrix}\right| a_{11} & a_{12} \\ b_{21} & b_{22} \end{vmatrix} \begin{matrix} -b_{11} & -b_{12} \\ a_{21} & a_{22} \end{vmatrix};$$

for the third order,

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} + \begin{vmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{vmatrix}$$

$$= \begin{vmatrix} \left[\begin{matrix}\pm\\+\\\pm\end{matrix}\right| a_{11} & a_{12} & a_{13} \\ b_{21} & b_{22} & b_{23} \\ . & . & . \end{vmatrix} \begin{matrix} . & . & . \\ a_{21} & a_{22} & a_{23} \\ b_{31} & b_{32} & b_{33} \end{vmatrix} \begin{matrix} b_{11} & b_{12} & b_{13} \\ . & . & . \\ a_{31} & a_{32} & a_{33} \end{matrix};$$

[3] Many other specific forms may be given to the matrix, *e.g.*, for the fourth order we may write

$$\left\| \begin{matrix} a_1 & . & b_2 & . \\ b_1 & . & . & a_4 \\ . & b_2 & a_3 & . \\ . & a_2 & . & b_4 \end{matrix} \right\|;$$

and in general, in a matrix $||t_{ij}||_n$ if we select elements

$$t_{i_1 j_1},\ t_{i_1 j_2},\ t_{i_2 j_2},\ t_{i_2 j_3},\ t_{i_3 j_3},\ \ldots,\ t_{i_n j_n},\ t_{i_n j_1},$$

where all the i's are different and all the j's are different, and make all the other elements zeros, then a transversal (a set of elements one from each row and column) which does not contain a zero, must consist, either of $t_{i_1 j_1}, t_{i_2 j_2}, \ldots, t_{i_r j_r}$ or else of $t_{i_2 j_2}, t_{i_3 j_3}, \ldots, t_{i_n j_n}$. Then we make $t_{i_\mu j_\mu} = a_{j_\mu}$, and $t_{i_\nu j_{\nu+1}} = b_{j_{\nu+1}}$. The specific form adopted in the text seems the most convenient.

[4] The symbol "$\left[\begin{matrix}\pm\\+\\\pm\end{matrix}\right.$" prefixed to a 3-way determinant means that the first and third directions are to be signant, the second direction nonsignant. Thus

$$\left[\begin{matrix}\pm\\+\\\pm\end{matrix}\right| \begin{matrix} t_{111} & t_{113} \\ t_{121} & t_{123} \end{matrix} \left| \begin{matrix} t_{211} & t_{213} \\ t_{221} & t_{223} \end{matrix} \right. = t_{111}\, t_{223} - t_{113}\, t_{221} - t_{211}\, t_{123} + t_{213}\, t_{121}.$$

It will be observed that the a's and b's are so disposed in the 3-way matrix that their indices correspond to the second and third indices of the t's. This

and generally, for the nth order,

$$\begin{vmatrix} a_{11} & \cdots & a_{1n} \\ \cdots & \cdots & \cdots \\ a_{n1} & \cdots & a_{nn} \end{vmatrix} + \begin{vmatrix} b_{11} & \cdots & b_{1n} \\ \cdots & \cdots & \cdots \\ b_{n1} & \cdots & b_{nn} \end{vmatrix}$$

$$= \begin{bmatrix} \pm \\ + \\ \pm \end{bmatrix} \begin{vmatrix} a_{11} & \cdots & \cdot & \cdots & \cdot & \cdots & \cdot\ \cdot\ \cdot & \cdot & \cdots & (-1)^{n-1}b_{11}\cdots \\ b_{21} & \cdots & a_{21} & \cdots & \cdot & \cdots & \cdot\ \cdot\ \cdot & \cdot & \cdots & \cdot & \cdots \\ \cdot & \cdots & b_{31} & \cdots & a_{31} & \cdots & \cdot\ \cdot\ \cdot & \cdot & \cdots & \cdot & \cdots \\ \cdots & & \cdots & & \cdots & & \cdot\ \cdot\ \cdot & \cdots & & \cdots & \\ \cdot & \cdots & \cdot & \cdots & \cdot & \cdots & \cdot\ \cdot\ \cdot & a_{n-1,1}\cdots & & \cdot & \cdots \\ \cdot & \cdots & \cdot & \cdots & \cdot & \cdots & \cdot\ \cdot\ \cdot & b_{n1} & \cdots & a_{n1} & \cdots \end{vmatrix} \quad (2)$$

Again, if A and B are determinants of three dimensions with the second index nonsignant, their sum may be expressed as a 4-way determinant with the second and third indices non-signant. For the second order,[8]

$$\begin{bmatrix} \pm \\ + \\ \pm \end{bmatrix} \begin{vmatrix} a_{111} & a_{112} & a_{211} & a_{212} \\ a_{121} & a_{122} & a_{221} & a_{222} \end{vmatrix} + \begin{bmatrix} \pm \\ + \\ \pm \end{bmatrix} \begin{vmatrix} b_{111} & b_{112} & l_{\cdot\cdot\cdot} & l_{\cdot\cdot\cdot} \\ b_{121} & b_{122} & l_{\cdot\cdot\cdot} & l_{\cdot\cdot\cdot} \end{vmatrix}$$

$$= \begin{bmatrix} \pm \\ + \\ + \\ \pm \end{bmatrix} \begin{vmatrix} a_{111} & a_{112} & b_{211} & b_{212} \\ a_{121} & a_{122} & b_{221} & b_{222} \\ \hline -b_{111} & -b_{112} & a_{211} & a_{212} \\ -b_{121} & -b_{122} & a_{221} & a_{222} \end{vmatrix};$$

conforms to the arrangement in (1), where the single index of each a and each b corresponds to the number of the column.

If we wish to obtain as the sum of A and B a 3-way determinant of signancy $[+\pm\pm]$, *i.e.*, to have the first index nonsignant, the matrix would differ from that in the text simply by omission of the sign-factor $(-1)^{n-1}$. From here on, the possibilities arising from differences in respect to signancy become more numerous. We therefore proceed in the text to give but one example in which A and B are determinants of three dimensions, and then pass to the general case of $p-1$ dimensions.

[8] The first index takes its two values in the upper and lower main divisions or layers of the 4-way matrix; the second index takes its two values in the left and right secondary divisions or 2-way sublayers; the third index takes its two values in the upper and lower rows of each 2-way sublayer; and the fourth index takes its two values in the left and right elements of each row.

for the third order,

$$\left[\begin{matrix}\pm\\+\\\pm\end{matrix}\right]\begin{vmatrix} a_{111} & a_{112} & a_{113} & a_{211} & a_{212} & a_{213} & a_{311} & a_{312} & a_{313} \\ a_{121} & a_{122} & a_{123} & a_{221} & a_{222} & a_{223} & a_{321} & a_{322} & a_{323} \\ a_{131} & a_{132} & a_{133} & a_{231} & a_{232} & a_{233} & a_{331} & a_{332} & a_{333} \end{vmatrix}$$

$$+\left[\begin{matrix}\pm\\+\\\pm\end{matrix}\right]\begin{vmatrix} b_{111} & b_{112} & b_{113} & b_{211} & b_{212} & b_{213} & b_{311} & b_{312} & b_{313} \\ b_{121} & b_{122} & b_{123} & b_{221} & b_{222} & b_{223} & b_{321} & b_{322} & b_{323} \\ b_{131} & b_{132} & b_{133} & b_{231} & b_{232} & b_{233} & b_{331} & b_{332} & b_{333} \end{vmatrix}$$

$$=\left[\begin{matrix}\pm\\+\\+\\\pm\end{matrix}\right]\begin{vmatrix} a_{111} & a_{112} & a_{113} & b_{211} & b_{212} & b_{213} & \cdot & \cdot & \cdot \\ a_{121} & a_{122} & a_{123} & b_{221} & b_{222} & b_{223} & \cdot & \cdot & \cdot \\ a_{131} & a_{132} & a_{133} & b_{231} & b_{232} & b_{233} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & a_{211} & a_{212} & a_{213} & b_{311} & b_{312} & b_{313} \\ \cdot & \cdot & \cdot & a_{221} & a_{222} & a_{223} & b_{321} & b_{322} & b_{323} \\ \cdot & \cdot & \cdot & a_{231} & a_{232} & a_{233} & b_{331} & b_{332} & b_{333} \\ b_{111} & b_{112} & b_{113} & \cdot & \cdot & \cdot & a_{311} & a_{312} & a_{313} \\ b_{121} & b_{122} & b_{123} & \cdot & \cdot & \cdot & a_{321} & a_{322} & a_{323} \\ b_{131} & b_{132} & b_{133} & \cdot & \cdot & \cdot & a_{331} & a_{332} & a_{333} \end{vmatrix}$$

and generally, for the nth order,[6] (3)

$$\left|a^{\pm+\pm}_{a_1 a_2 a_3}\right|_n + \left|b^{\pm+\pm}_{\beta_1 \beta_2 \beta_3}\right|_n =$$

$$\left[\begin{matrix}\pm\\+\\+\\\pm\end{matrix}\right]\begin{vmatrix} a_{111}\ \ldots & b_{211}\ \ldots & \cdot & \cdot & \cdot \\ \ldots\ \ldots & \ldots\ \ldots & & & \\ \cdot & a_{211}\ \ldots & b_{311}\ \ldots & \cdot & \cdot \\ & \ldots\ \ldots & \ldots\ \ldots & & \\ \cdot & \cdot & a_{311}\ \ldots & \cdot & \cdot \\ & & \ldots\ \ldots & & \\ & & & & \\ \cdot & \cdot & \cdot & a_{n-1,11}\ \ldots & b_{n11}\ \ldots \\ & & & \ldots\ \ldots & \ldots\ \ldots \\ (-1)^{n-1}b_{111}\ \ldots & \cdot & \cdot & \cdot & a_{n11}\ \ldots \\ \ldots\ \ldots & & & & \ldots\ \ldots \end{vmatrix}$$

[6] The symbols + and ± are written above the indices $a_1\ a_2\ a_3$ and $\beta_1\ \beta_2\ \beta_3$ in lieu of the symbols $\cup$ and $\cap$ heretofore used to mean "nonsignant" and "signant." Each index beyond β is signant or nonsignant on the right, according as it is signant or nonsignant on the left, as stated in the previous paper; and in every determinant there must be an even number of signant indices.

4. In each of the foregoing cases the matrix of Δ is constructed by taking the layers of the first direction of the matrix of A, in their natural order, as the sublayers $11, 22, \ldots nn$ of the first and second directions of the matrix of Δ, and the layers of the first direction of the matrix of B, in their natural order, as the sublayers $n1, 12, \ldots, n-1, n$ of the first and second directions of the matrix of Δ, and filling the remaining places in the matrix with zeros.[7]

In the general case, where A and B are of $p-1$ dimensions, we write

$$\| \Delta \| = \| t_{\alpha\beta\gamma\cdots\lambda} \|_n^{(p)} =$$

$$\begin{Vmatrix} \| t_{11\gamma\cdots\lambda} \|_n^{(p-2)} & \| t_{12\gamma\cdots\lambda} \|_n^{(p-2)} & \cdots & \| t_{1n\gamma\cdots\lambda} \|_n^{(p-2)} \\ \| t_{21\gamma\cdots\lambda} \|_n^{(p-2)} & \| t_{22\gamma\cdots\lambda} \|_n^{(p-2)} & \cdots & \| t_{2n\gamma\cdots\lambda} \|_n^{(p-2)} \\ \cdots & \cdots & \cdots & \cdots \\ \| t_{n1\gamma\cdots\lambda} \|_n^{(p-2)} & \| t_{n2\gamma\cdots\lambda} \|_n^{(p-2)} & \cdots & \| t_{nn\gamma\cdots\lambda} \|_n^{(p-2)} \end{Vmatrix}_n^{(p)} \tag{4}$$

$$= \begin{Vmatrix} \| a_{1\gamma\cdots\lambda} \| & \| b_{2\gamma\cdots\lambda} \| & \cdot & \cdots & \cdot & \cdot \\ \cdot & \| a_{2\gamma\cdots\lambda} \| & \| b_{3\gamma\cdots\lambda} \| & \cdots & \cdot & \cdot \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdot & \cdot & \cdot & \cdots & \| a_{n-1\gamma\cdots\lambda} \| & \| b_{n\gamma\cdots\lambda} \| \\ \| b_{1\gamma\cdots\lambda} \| & \cdot & \cdot & \cdots & \cdot & \| a_{n\gamma\cdots\lambda} \| \end{Vmatrix}_n^{(p)}$$

Evidently all of the $n!$ $(p-1)$-way components of this matrix (taken with respect to the first and second directions), except two, will consist of zero elements; these two will be identical with the matrices of A and B.

5. It remains to see what signancy should be given to Δ for any given signancy of A and B, and in what cases the elements of $\| b_{1\gamma\cdots\lambda} \|$[8] in Δ should carry a negative sign. These points are settled by the formulas[9] for the decomposition of a p-way determinant into a sum of $(p-1)$-way determinants or perma-

[7] One may easily satisfy oneself that zeros must be everywhere used, in the general form, since the cofactor of each remaining place does not vanish.

[8] Any other sublayer of b's might, of course, carry the sign factor.

[9] Given on p. 247 of the paper mentioned in Note 1.

nents (as the case may be) and for the decomposition of a p-way permanent into a sum of $(p-1)$-way permanents. For the matrix (4), with the elements of $\| b_{1\gamma \ldots \lambda} \|$ of positive sign, these formulas become:

$$|t^{\pm\pm}_{\alpha\beta} \ldots|^{(p)}_{n} = |a^{+}_{\beta} \ldots|^{(p-1)}_{n} + (-1)^{n-1} |b^{+}_{\beta} \ldots|^{(p-1)}_{n}, \tag{5}$$

$$|t^{\pm+}_{\alpha\beta} \ldots|^{(p)}_{n} = |a^{\pm}_{\beta} \ldots|^{(p-1)}_{n} + (-1)^{n-1} |b^{\pm}_{\beta} \ldots|^{(p-1)}_{n}, \tag{6}$$

$$|t^{+\pm}_{\alpha\beta} \ldots|^{(p)}_{n} = |a^{\pm}_{\beta} \ldots|^{(p-1)}_{n} + |b^{\pm}_{\beta} \ldots|^{(p-1)}_{n}, \tag{7}$$

$$|t^{++}_{\alpha\beta} \ldots|^{(p)}_{n} = |a^{+}_{\beta} \ldots|^{(p-1)}_{n} + |b^{+}_{\beta} \ldots|^{(p-1)}_{n}. \tag{8}$$

For example, when (8) is written for the case of $p=2$, *viz.*:

$$|t^{++}_{\alpha\beta}| = |a^{+}_{\beta}| + |b^{+}_{\beta}|,$$

and when (5) is written for the case of $p=2$, *viz.*:

$$|t^{\pm\pm}_{\alpha\beta}| = |a^{+}_{\beta}| + (-1)^{n-1} |b^{+}_{\beta}|,$$

then we have the relations that were given in (1), the sign factor being there absorbed into Δ.

Again, when (6) is written for the case of $p=3$, with γ signant, *viz.*:

$$|t^{\pm+\pm}_{\alpha\beta\gamma}| = |a^{\pm\pm}_{\beta\gamma}| + (-1)^{n-1} |b^{\pm\pm}_{\beta\gamma}|,$$

then we have the relation that was given in (2). And when (6) is written for the case of $p=4$, with γ nonsignant and δ signant, *viz.*:

$$|t^{\pm+\pm}_{\alpha\beta\gamma\delta}| = |a^{\pm+\pm}_{\beta\gamma\delta}| + (-1)^{n-1} |b^{\pm+\pm}_{\beta\gamma\delta}|,$$

we have the relation that was given in (3).

If the matrix of (4) be designated by M, and that obtained from (4) by prefixing $(-1)^{n-1}$ to every element of the sublayer $||b_{1\gamma \ldots \lambda}||$ by M', then the foregoing results may be summarized as in the next section.

6. If A and B are determinants which have the first index nonsignant, their sum may be expressed (*i*) as a determinant Δ of matrix M having the first and second indices nonsignant, the signancy of the remaining indices being continued (as is the case throughout); or (*ii*) a determinant Δ of matrix M' having the first and second indices signant. And the sum of

two permanents may be expressed (*i*) as a permanent of matrix M, or (*ii*) as a determinant of matrix M' having the first two indices, and only these, signant. If A and B are determinants of an odd number of dimensions, with only the first index nonsignant, this rule enables us to express their sum either as a determinant of matrix M with the first and second indices nonsignant and all the rest signant, or as a determinant of matrix M' with all the indices signant.

If, on the other hand, A and B have the first index signant, their sum may be expressed (*i*) as a determinant Δ of matrix M having the first index nonsignant and the second index signant, or (*ii*) as a determinant Δ of matrix M' having the first index signant and the second index nonsignant.

7. Four determinants of $p-2$ dimensions may evidently be so added as to form a determinant of p dimensions; and in general 2^ν determinants of $p-\nu$ dimensions may be thus added. It will be sufficient to give as two illustrations the sums of four 2-way determinants of orders 2 and 3 respectively.

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} + \begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix} + \begin{vmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{vmatrix} + \begin{vmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{vmatrix}$$

$$= \begin{bmatrix} \pm \\ + \\ \pm \end{vmatrix} \begin{matrix} a_{11} & a_{12} \\ b_{21} & b_{22} \end{matrix} \begin{vmatrix} -d_{11} & -d_{12} \\ c_{21} & c_{22} \end{vmatrix} \\ \hline \begin{vmatrix} -c_{11} & -c_{12} \\ -d_{21} & -d_{22} \end{vmatrix} \begin{vmatrix} -b_{11} & -b_{12} \\ a_{21} & a_{22} \end{vmatrix} \end{bmatrix};$$

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} + \ \ldots \ + \begin{vmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \end{vmatrix}$$

$$= \begin{bmatrix} \pm \\ + \\ \pm \end{vmatrix} \begin{matrix} a_{11} & a_{12} & a_{13} \\ b_{21} & b_{22} & b_{23} \\ \cdot & \cdot & \cdot \end{matrix} \begin{vmatrix} \cdot & \cdot & \cdot \\ c_{21} & c_{22} & c_{23} \\ d_{31} & d_{32} & d_{33} \end{vmatrix} \begin{vmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix} \\ \hline \begin{matrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{matrix} \begin{vmatrix} \cdot & \cdot & \cdot \\ a_{21} & a_{22} & a_{23} \\ b_{31} & b_{32} & b_{33} \end{vmatrix} \begin{vmatrix} d_{11} & d_{12} & d_{13} \\ \cdot & \cdot & \cdot \\ c_{31} & c_{32} & c_{33} \end{vmatrix} \\ \hline \begin{vmatrix} c_{11} & c_{12} & c_{13} \\ d_{21} & d_{22} & d_{23} \\ \cdot & \cdot & \cdot \end{vmatrix} \begin{vmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix} \begin{vmatrix} b_{11} & b_{12} & b_{13} \\ \cdot & \cdot & \cdot \\ a_{31} & a_{32} & a_{33} \end{vmatrix} \end{bmatrix}.$$

A NEW TYPE OF INTEGRAL EXPANSION

By NORBERT WIENER

Let $f(x)$ be developable into the Taylor series,

$$f(x)=f(u)+(x-u)f'(u)+\ \dots\ +\frac{(x-u)^n}{n!}f^{(n)}(u)+\ \dots, \qquad (1)$$

which we shall suppose uniformly convergent in the real argument u over the entire interval $-1\leq u\leq 1$ for every x such that $-1\leq x\leq 1$. Let $G(u)$ be any function bounded and summable over the interval $-1\leq u\leq 1$. Then

$$f(x)\int_{-1}^{1}G(u)du=\int_{-1}^{1}f(u)G(u)du+\int_{-1}^{1}(x-u)f'(u)G(u)du+\ \dots$$

$$+\frac{1}{[n!}\int_{-1}^{1}(x-u)^n f^{(n)}(u)G(u)du+\ \dots \qquad (2)$$

Now let us suppose that $G(u)$ together with its derivatives of all orders is continuous over the interval $(-1, 1)$, and that it vanishes with all its derivatives for $u=\pm 1$. Then, integrating by parts,

$$\int_{-1}^{1}(x-u)^n f^{(n)}(u)G(u)du=\int_{u=-1}^{u=1}(x-u)^n G(u)d\left\{f^{(n-1)}(u)\right\}$$

$$=\left[(x-u)^n G(u)f^{(n-1)}(u)\right]_{-1}^{1}-\int_{u=-1}^{u=1}f^{(n-1)}(u)d\left\{(x-u)^n G(u)\right\}$$

$$=-\int_{-1}^{1}\frac{d}{du}\left\{(x-u)^n G(u)\right\}f^{(n-1)}(u)du$$

$$=-\int_{u=-1}^{u=1}\frac{d}{du}\left\{(x-u)^n G(u)\right\}d\left\{f^{(n-2)}(u)\right\}$$

$$=-\left\{\frac{d}{du}\left[(x-u)^n G(u)\right]f^{(n-2)}(u)\right\}_{-1}^{1}$$

$$+\int_{u=-1}^{u=1} f^{(n-2)}(u)d\left\{\frac{d}{du}\left[(x-u)^n G(u)\right]\right\}$$

$$=\int_{-1}^{1}\frac{d^2}{du^2}\left[(x-u)^n G(u)\right]f^{(n-2)}(u)du=\ \ldots$$

$$=(-1)^n\int_{-1}^{1}\frac{d^n}{du^n}\left[(x-u)^n G(u)\right]f(u)du$$

$$=\int_{-1}^{1}\frac{d^n}{du^n}\left[(u-x)^n G(u)\right]f(u)du. \tag{3}$$

We shall now assume that $\int_{-1}^{1} G(u)du \neq 0$. We consequently obtain from (2) and (3) the formula

$$f(x)=\frac{1}{\int_{-1}^{1}G(u)du}\left\{\int_{-1}^{1}G(u)f(u)du\right.$$

$$+\int_{-1}^{1}\frac{d}{du}\left[(u-x)G(u)\right]f(u)du+\ \ldots$$

$$\left.+\frac{1}{n!}\int_{-1}^{1}\frac{d^n}{du^n}\left[(u-x)^n G(u)\right]f(u)du+\ \ldots\right\} \tag{4}$$

Let us write $F(u)$ for $\int_{-1}^{u} G(u)du$. $F(u)$ will then be characterized by the same properties as those we have determined for $G(u)$ as to the existence and continuity of its derivatives, and as to the vanishing of the function and its derivatives at the end of the interval, except that $F(1)\neq 0$. Let us consider the expression $\frac{1}{n!}\frac{d^{n+1}}{du^{n+1}}\left[(u-x)^n F(u)\right]$. Clearly,

$$\frac{1}{n!}\frac{d^{n+1}}{du^{n+1}}\left[(u-x)^n F(u)\right]=\frac{1}{n!}\frac{d}{du^n}\frac{d}{du}\left[(u-x)^n F(u)\right]$$

$$=\frac{1}{n!}\frac{d^n}{du^n}\left[n(u-x)^{n-1}F(u)+(u-x)^n G(u)\right]$$

$$= \frac{1}{(n-1)!}\frac{d^n}{du^n}\left[(u-x)^{(n-1)}F(u)\right]+\frac{1}{n!}\frac{d^n}{du^n}\left[(u-x)^nG(u)\right]$$

$$= \frac{1}{(n-2)!}\frac{d^{n-1}}{du^{n-1}}\left[(u-x)^{n-2}F(u)\right]+\frac{1}{(n-1)!}\frac{d^{n-1}}{du^{n-1}}\left[(u-x)^{n-1}G(u)\right]$$

$$+\frac{1}{n!}\frac{d^n}{du^n}\left[(u-x)^nG(u)\right]$$

$$=G(u)+\frac{d}{du}\left[(u-x)G(u)\right]+\ \ldots\ +\frac{1}{n!}\frac{d^n}{du^n}\left[(u-x)^nG(u)\right]. \quad (5)$$

Hence (4) becomes

$$f(x)=\lim_{n\to\infty}\frac{1}{n!\,F(1)}\int_{-1}^{1}\frac{d^{n+1}}{du^{n+1}}\left[(u-x)^nF(u)\right]f(u)du. \quad (6)$$

If we take for our $G(x)$ an even function, and if $f(x)$ is even, (6) becomes

$$f(x)=\lim_{n\to\infty}\frac{1}{n!F(1)}\int_{0}^{1}\frac{d^{n+1}}{du^{n+1}}\left\{\left[(u-x)^n+(u+x)^n\right]F(u)\right\}f(u)du. \quad (6a)$$

Formulæ (6) and (6a) belong to the type

$$f(x)=\lim_{n\to\infty}\int_a^b K_n\,(x,u)f(u)du, \quad (7)$$

to which belong also the Fourier series expansion, one form of the Fourier integral expansion, and many other analogous developments. In the more familiar of these, a sufficient condition even for the uniform validity of the expansion in question only involves the existence and continuity of a finite number of derivatives of f, together perhaps with particular restrictions on f at the ends of the interval of integration. On the other hand, we have only established the validity of (6a) for functions which are analytic with a certain uniformity over the interval $(-1, 1)$, and which are even.

I wish to show that if we take as our $G(u)$ the function $e^{\frac{1}{u^2-1}}$, the difference between (6a) and an expansion of the Fourier type is really essential. In particular, I wish to show that if $f(x)$ is

bounded and absolutely summable over $(0, 1-\epsilon)$, is zero over $(1-\epsilon, 1)$, and satisfies (6a) at every point of $(0, 1)$, then it is identically zero over $(0, 1)$. From this it will follow at once that a function satisfying (6a) over $(0,1)$, bounded, and absolutely summable, is completely characterized by its values in the neighborhood of 1. It is not even necessary, however, that the function satisfy (6a) over the whole of $(0, 1)$; it is enough that

$$\lim_{n\to\infty} \frac{2}{n!F(1)} \int_0^1 \frac{d^{n+1}}{du^{n+1}}[u^n F(u)]f(u)du$$

exist.

We introduce the auxiliary function of a complex variable,

$$\phi(\xi) = \frac{2\xi}{\int_{-1}^{1} e^{\frac{1}{x^2-1}}dx} \int_0^{1-\epsilon} e^{\frac{1}{\xi^2u^2-1}} f(u)du, \tag{8}$$

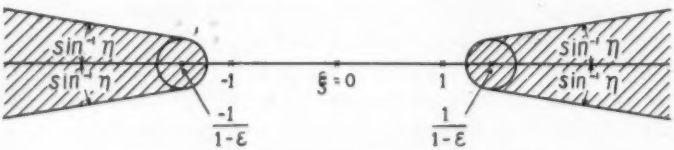
and proceed to investigate its singularities. To begin with,

$$\left| exp\left(\frac{1}{\xi^2u^2-1}\right)\right| \leq exp\left|\frac{1}{\xi^2u^2-1}\right|. \tag{9}$$

If now $|\xi u+1|>\eta$, $|\xi u-1|>\eta$, we have

$$\left| exp\left(\frac{1}{\xi^2u^2-1}\right)\right| < e^{\frac{1}{\eta^2}}. \tag{10}$$

Now, the region of the complex plane in which ξ lies when $|\xi u+1|>\eta$, $|\xi u-1|>\eta$ for every u in the interval $(0, 1-\epsilon)$ is the region unshaded in the following figure.



The Small Circles are of Radius $\frac{\eta}{1-\epsilon}$

In this unshaded region, $e^{\frac{1}{\xi^2u^2-1}} f(u)$ is uniformly bounded and

summable in u, so that $\phi(\xi)$ is defined. The related function

$$\phi'(\xi)=\frac{2}{\int_{-1}^{1} e^{\frac{1}{x^2-1}}dx}\int_0^{1-\epsilon} e^{\frac{1}{\xi^2u^2-1}} f(u)du$$

$$-\frac{4\xi^2}{\int_{-1}^{1} e^{\frac{1}{x^2-1}}dx}\int_0^{1-\epsilon}\frac{u^2}{(\xi^2u^2-1)^2}e^{\frac{1}{\xi^2u^2-1}} f(u)du$$

may be proved to exist by a similar argument over the same unshaded region. There is no difficulty in showing directly that

$$\lim_{|\epsilon|\to 0}\frac{\phi(\xi+\lambda)-\phi(\xi)}{\lambda}=\phi'(\xi),$$

whenever ξ and $\xi+\lambda$ lie in the unshaded region. Hence ϕ is analytic over this region.

Now let us consider $\phi\left(\frac{x}{1-y}\right)$ as a function of y, given that $|x|<1/(1-\epsilon)$. It is clearly analytic in a neighborhood containing the origin, as is also $\frac{1}{1-y}\phi\left(\frac{x}{1-y}\right)$. Let us put

$$\int_0^z \phi(z)dz=\Phi(z),$$

where the path of integration lies entirely within the circle of convergence of the Taylor series about the origin for $\phi(x)$. We shall then have

$$\frac{1}{1-y}\phi\left(\frac{x}{1-y}\right)=\frac{\partial}{\partial x}\Phi\left(\frac{x}{1-y}\right)=\left[\frac{\partial}{\partial x}\Phi\left(\frac{x}{1-y}\right)\right]_{y=0} \tag{11}$$

$$+y\left[\frac{\partial^2}{\partial x\partial y}\Phi\left(\frac{x}{1-y}\right)\right]_{y=0}+\ldots+\frac{y^n}{n!}\left[\frac{\partial^{n+1}}{\partial x\partial y^n}\Phi\left(\frac{x}{1-y}\right)\right]_{y=0}+\ldots$$

Now let $\frac{x}{1-y}=z$, or $z=x+yz$. Then

$$\frac{\partial z}{\partial y}=\frac{x}{(1-y)^2}=\frac{x}{1-y}\left(\frac{1}{1-y}\right)=z\frac{\partial z}{\partial x}. \tag{12}$$

Hence,

$$\frac{\partial \Phi(z)}{\partial y}=\Phi'(z)\frac{\partial z}{\partial y}=z\Phi'(z)\frac{\partial z}{\partial x}=z\frac{\partial \Phi(z)}{\partial x}. \tag{13}$$

Again,

$$\begin{aligned}\frac{\partial^2\Phi(z)}{\partial y}&=\frac{\partial}{\partial y}\left(z\frac{\partial \Phi(z)}{\partial x}\right)=\frac{\partial z}{\partial y}\frac{\partial \Phi(z)}{\partial x}+z\frac{\partial^2\Phi(z)}{\partial x\partial y}\\ &=\Phi'(z)\frac{\partial z}{\partial y}\frac{\partial z}{\partial x}+z\frac{\partial^2\Phi(z)}{\partial x\partial y}\\ &=\frac{\partial \Phi(z)}{\partial y}\frac{\partial z}{\partial x}+z\frac{\partial^2\Phi(z)}{\partial x\partial y}\\ &=\frac{\partial}{\partial x}\left(z\frac{\partial \Phi(z)}{\partial y}\right)=\frac{\partial}{\partial x}\left(z^2\frac{\partial \Phi(z)}{\partial x}\right).\end{aligned} \tag{14}$$

In general,

$$\frac{\partial^n \Phi(z)}{\partial y^n}=\frac{\partial^{n-1}}{\partial x^{n-1}}\left(z^n\frac{\partial \Phi(z)}{\partial x}\right). \tag{15}$$

Hence,

$$\left[\frac{\partial^{n+1}\Phi(z)}{\partial x\partial y^n}\right]_{y=0}=\left[\frac{\partial^n}{\partial x^n}\left(z^n\frac{\partial \Phi(z)}{\partial x}\right)\right]_{y=0}=\frac{\partial^n}{\partial x^n}\left[x^n\phi(x)\right]. \tag{16}$$

Formula (11) thus becomes

$$\begin{aligned}\frac{1}{1-y}\phi\left(\frac{x}{1-y}\right)&=\phi(x)+y\frac{d}{dx}\left(x\Phi(x)\right)+\cdots\\ &\quad+\frac{y^n}{n!}\frac{d^n}{dx^n}\left(x^n\phi(x)\right)+\cdots\end{aligned} \tag{17}$$

This is essentially a particular case of Lagrange's theorem, and the method of proof here employed is that found in Williamson's *Differential Calculus*. It has been given here *in extenso* simply

for the purpose of showing that there is actually a region for which the two sides of (17) are identical, provided that as in the present case the radius of convergence of the Maclaurin series for $\phi(x)$ is greater than 1.

I now say that if $\lim_{n\to\infty} \frac{1}{n!}\left[\frac{d^n}{dx^n}(x^n\phi(x))\right]_{x=1}$ exists, $\phi(x)$ is identically zero. To establish this, a consideration of the singularities of ϕ is sufficient. To begin with, ϕ is an odd function, and its singularities always occur in pairs $\pm\Xi$. Again, we have already seen that all the singularities of ϕ lie on the real axis, with a modulus greater than $\frac{1}{1-\epsilon}$. Now, since we may write (17) in the form

$$\phi\left(\frac{1}{1-y}\right) = \phi(1) + y\left\{\left[\frac{d}{dx}(x\phi(x))\right]_{x=1} - \phi(1)\right\} + \ldots$$
$$+ y^n\left\{\frac{1}{n!}\left[\frac{d^n}{dx^n}(x^n\phi(x))\right]_{x=1} - \frac{1}{(n-1)!}\left[\frac{d^{n-1}}{dx^{n-1}}(x^{n-1}\phi(x))\right]_{x=1}\right\} + \ldots, \tag{18}$$

and since this power-series converges for $y=1$, it follows that ϕ has no singularities on the finite positive real axis, and hence no singularities on the real axis at all, except possibly at infinity. The singularity at infinity, if there be any, must be a pole or essential singularity, for a function with only one singularity must be single-valued.

Let $y \to 1$ along any path for which $\arg\left(\frac{1}{1-y}\right)$ lies between $-\sin^{-1}\eta$ and $+\sin^{-1}\eta$. Since power-series (18) converges to $\lim_{n\to\infty} \frac{1}{n!}\left[\frac{d^n}{dx^n}(x^n\phi(x))\right]_{x=1}$, if this quantity exists, it follows from a theorem of Stolz[1] that

$$\lim_{y\to 1} \phi\left(\frac{1}{1-y}\right) = \lim_{n\to\infty} \frac{1}{n!}\left[\frac{d^n}{dx^n}(x^n\phi(x))\right]_{x=1}.$$

[1] O. Stolz, "Beweis einiger Sätze über Potenzreihen," *Zeitschrift für Math.*, Jahrgang 20, 1875, pp. 369–376; "Nachtrag . . .," ibid., Jahrgang 29, 1884, pp. 127–128.

$\lim_{y\to 1}\phi\left(\frac{1}{1-y}\right)$ will also exist if $y\to 1$ for any path for which $\arg\left(\frac{1}{1-y}\right)$ lies between $\pi-\sin^{-1}\eta$ and $\pi+\sin^{-1}\eta$, since ϕ is odd.

Now consider the function $\frac{\phi(\xi)}{\xi}$. This has no singularity at the origin, and is uniformly bounded whenever $\arg(\xi)$ lies outside of the angles $(-\sin^{-1}\eta, \sin^{-1}\eta)$ and $(\pi-\sin^{-1}\eta, \pi+\sin^{-1}\eta)$. All this follows from the uniformly bounded and summable character of $e^{\frac{1}{\xi^{-u^2-1}}}f(u)$. On the other hand, it follows from what we have just seen that if $\xi\to\infty$ along any path within the angles $(-\sin^{-1}\eta, \sin^{-1}\eta)$ and $(\pi-\sin^{-1}\eta, \pi+\sin^{-1}\eta)$, then $\lim_{\xi\to\infty}\frac{\phi(\xi)}{\xi}=0$. It follows that $\frac{\phi(\xi)}{\xi}$ can neither have a pole nor an essential singularity anywhere, and so reduces to a constant, which can only be zero. Hence, $\phi(\xi)\equiv 0$.

Now let $F(u)=\sum_0^\infty a_m u^m$. Then

$$
\left.\begin{aligned}
G(u) &= \sum_0^\infty m a_m u^{m-1} \\
\phi(\xi) &= \frac{2\xi}{F(1)}\int_0^{1-\epsilon}\left\{\sum_0^\infty m a_m(\xi u)^{m-1}\right\} f(u)du \\
&= \sum_0^\infty \frac{2\xi^m}{F(1)}\int_0^{1-\epsilon} m a_m u^{m-1} f(u)du \qquad \left[|\xi|<\frac{1}{1-\epsilon}\right] \\
\frac{1}{n!}\left[\frac{d^n}{dx^n}(x^n\phi(x))\right]_{x=1} &= \left\{\sum_0^\infty \frac{2(m+n)(m+n-1)\dots(m+1)m}{n!F(1)}\right. \\
&\qquad \left. x^m\int_0^{1-\epsilon} a_m u^{m-1} f(u)\,du\right\}_{x=1} \\
&= \frac{2}{n!\,F(1)}\int_0^{1-\epsilon}\frac{d^{n+1}}{du^{n+1}}\left[u^n F(u)\right] f(u)du.
\end{aligned}\right\} \quad (19)
$$

That is, the validity of (6a) for $x=0$ involves the identical vanishing of $\phi(\xi)$. In other words, if (6a) holds,

$$\int_0^{1-\epsilon} e^{\frac{1}{\xi^2 u^2-1}} f(u)du \equiv 0, \tag{20}$$

for every value of ξ.

Let us now consider the sequence of derivatives of $e^{\frac{1}{\xi^2u^2-1}}$. To this end, let us first consider the derivatives of $e^{\frac{1}{x-1}}$. Its first derivative is $\frac{-1}{(x-1)^2}e^{\frac{1}{x-1}}$, its second derivative

$$\left[\frac{2}{(x-1)^3}+\frac{1}{(x-1)^4}\right]e^{\frac{1}{x-1}}.$$

In each of these cases, the derivative is of the form

$$\left[\frac{2A_1}{x-1}+\frac{2A_2}{(x-1)^2}+\ldots+\frac{2A_{2n-1}}{(x-1)^{2n-1}}\pm\frac{1}{(x-1)^{2n}}\right]e^{\frac{1}{x-1}},$$

where the A's are positive or negative integers. If we differentiate this expression we get

$$\left[\frac{-2A_1}{(x-1)^2}-\frac{4A_2}{(x-1)^3}-\ldots\mp\frac{2n}{(x-1)^{2n+1}}-\frac{2A_1}{(x-1)^3}\right.$$
$$\left.-\ldots-\frac{2A_{2n-1}}{(x-1)^{2n+1}}\mp\frac{1}{(x-1)^{2n+2}}\right]e^{\frac{1}{x-1}},$$

which is of the same form. Hence, by mathematical induction, every derivative of $e^{\frac{1}{x-1}}$ is of this form. It follows that there is an integer k such that

$$\left[\frac{d^n}{dx^n}e^{\frac{1}{x-1}}\right]_{x=0}=\frac{2k+1}{e}\neq 0, \tag{21}$$

so that

$$\left[\frac{d^{2n}}{dx^{2n}}e^{\frac{1}{x-1}}\right]_{x=0}\neq 0, \tag{22}$$

as is obvious from a comparison of the Taylor series for $e^{\frac{1}{x-1}}$ and $e^{\frac{1}{x^2-1}}$.

It follows from (20) on differentiation that

$$0 = \int_0^{1-\epsilon} \left[\frac{\partial^{2n}}{\partial \xi^{2n}} \left(e^{\frac{1}{\xi^2 u^2 - 1}} \right) \right]_{\xi=0} f(u)du$$

$$= \int_0^{1-\epsilon} u^{2n} \left[\frac{d^{2n}}{dx^{2n}} e^{\frac{1}{x^2-1}} \right]_{x=0} f(u)du. \tag{23}$$

Hence, by (22)

$$\int_0^{1-\epsilon} u^{2n} f(u)du = 0 \tag{24}$$

for every integral value of n. It is a direct consequence from this and the fact that the even powers of u form a complete set over the interval $(0, 1-\epsilon)$—as follows from Weierstrass' theorem on polynomial representation—that except for a set of points of zero measure, $f(u) = 0$ over $(0, 1-\epsilon)$. From this and (6*a*) it again follows that $f(u) = 0$ everywhere over $(0, 1)$. This completes the proof of our theorem, and establishes the fact that if (6*a*) holds of a bounded and absolutely summable function, that function is completely determined by its values for real arguments in the neighborhood of 1.

NOTE ON EINSTEIN'S THEORY OF GRAVITATION

By H. B. PHILLIPS

1. It is the object of this paper to discuss the gravitational field about a mass particle by direct use of the equivalence principle without the tensor calculus.[1] In this way one can obtain a more concrete physical picture than that presented by the more mathematical method. Such a discussion, however, requires concrete interpretations of the fundamental hypotheses which may seem to include additional assumptions.

2. **Fundamental hypotheses.** In developing his theory of gravitation Einstein used three fundamental hypotheses.

(*A*) **The equivalence hypothesis.** Acceleration of the reference system is equivalent to gravitation.

This means that if an observer and his reference system, or laboratory, are accelerated, events seem to occur as in a gravitational field and in no way can he determine whether he is in a gravitational field or whether his reference system is merely accelerated. Thus, if the laboratory is accelerated upward objects press with greater force upon the floor as if subject to a gravitational force acting downward.

It is to be noticed that the acceleration of the reference system and the equivalent gravitation are oppositely directed. If the laboratory falls freely, its acceleration, having the same direction, annuls the action of the field and objects cease to have any apparent weight. Also it is in measurements on objects that do not directly experience his acceleration that the moving observer obtains the same results as the fixed observer on objects at rest in a gravitational field.

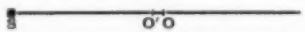
(*B*) **The infinitesimal hypothesis.** In the infinitesimal neighborhood of a world point (x, y, z, t) it is possible to choose a reference system with respect to which the restricted relativity is valid.

[1] A complete exposition of Einstein's theory is contained in A. S. Eddington's Report on the Relativity Theory of Gravitation, published by the Physical Society of London.

Such a reference system is called Galilean since Galileo first used the restricted form of relativity. It is assumed that a free particle moves at each point of its path like a point in a Galilean system at that point.

(*C*) **The general principle of relativity.** The laws of physics can be stated in a form that is the same for all reference systems. This condition is fulfilled by expressing the laws as relations between tensors. No use of it is made in this paper.

3. **The observer falling from infinity.** Consider a mass concentrated at a point S and a fixed observer F or series of fixed observers along a line through S.



Suppose a Galilean observer G starts from infinity and falls freely toward S. I assume that he will move along a straight line which we may take on the line of the fixed observers. When F and G are at the same point O, we wish to determine the relation between their measurements made on events occurring on the line near O.

The observer G is actually accelerated. The observer F is subject to gravitation which affects his measurements on fixed objects as if he were accelerated. Hence in passing from O to O' the measurements of F should be affected by gravitation in the same way those of G are affected by acceleration. At infinity both are Galilean observers at rest and so obtain the same measurements. Hence we conclude that, at all points of the line, *F and G obtain the same measure of a fixed length and the same interval of time at a fixed point.* It is to be noticed that this equality applies only to measurements made on objects in the fixed system; for, as stated above, the equivalence is with respect to objects that do not have the acceleration of the moving observer.

Let dr be the distance between two points of the line and dt the interval of time between events at those points as measured by F and dR, dT the corresponding quantities measured by G. I assume that these pairs of measurements will be connected by linear equations,

$$dr = AdR + BdT, \qquad dT = Cdr + Ddt. \tag{1}$$

To measure a fixed object the moving observer must determine the distance between the positions occupied by its ends at the same time ($dT=0$). Hence, from (1)

$$dr=AdR.$$

But in this case we must also have

$$dr=dR.$$

Hence

$$A=1. \tag{2}$$

To measure an interval of time at a fixed point we must place $dr=0$. Hence

$$dT=Ddt.$$

But in this case

$$dT=dt,$$

and so

$$D=1. \tag{3}$$

Substituting (2) and (3) in (1) and solving for dR, we get

$$\begin{aligned} dR&=(1-BC)\,dr-Bdt,\\ dT&=Cdr+dt. \end{aligned} \tag{4}$$

Choose units of measurement such that the velocity of light in the moving system is 1. Then

$$\begin{aligned} ds^2=dT^2-dR^2=(1-B^2)dt^2+2[B+C(1-B^2)]drdt\\ +[C^2-(1-BC)^2]dr^2. \end{aligned}$$

If events in the fixed system are symmetrical with respect to past and future time, this must have the same value whether dt is positive or negative. The coefficient of $drdt$ is then zero; that is,

$$B+C(1-B^2)=0,$$

whence

$$C=-\frac{B}{1-B^2}.$$

Let

$$B=-\sqrt{1-\gamma}$$

where γ is a function to be determined later. Then

$$C = \frac{\sqrt{1-\gamma}}{\gamma}.$$

Substituting these values of B and C in (4), we get

$$dR = \frac{1}{\gamma}\,dr + \sqrt{1-\gamma}\,dt,$$

$$dT = \frac{\sqrt{1-\gamma}}{\gamma}\,dr + dt. \tag{5}$$

Solving for dr and dt,

$$dr = dR - \sqrt{1-\gamma}\,dT,$$

$$dt = \frac{1}{\gamma}dT - \frac{1}{\gamma}\sqrt{1-\gamma}\,dR. \tag{6}$$

4. **The function γ.** So far we have treated the moving system as a point. Actually the Galilean system which verifies the equivalence principle in the neighborhood of a point to terms of the second order is a three-dimensional one each point of which falls separately toward S. Let O, P be fixed points at distance r from S as estimated by the falling observer, and O', P' fixed points at distance $r+dr$ from S. To the fixed observer OO' and PP' are fixed lines intersecting in S. The point in the moving system where G estimates S to be should appear to F to be on both these lines. Consequently that point should appear to F to be the fixed point S.

Substituting $dR=r$, $dt=0$ in the equation

$$dR = \frac{1}{\gamma}dr + \sqrt{1-\gamma}dt,$$

we find that the distance to S as estimated by F is γr.

If, now, we move from O to O', we have

$$OO' = dr = d(\gamma r),$$

whence

$$\gamma r = r - C, \qquad \gamma = 1 - \frac{C}{r}, \tag{7}$$

the negative sign being used since $\gamma < 1$.

From (5), a fixed point ($dr=0$) appears to the moving observer to have the velocity

$$V=\frac{dR}{dT}=\sqrt{1-\gamma}.$$

Hence,

$$\gamma=1-V^2. \tag{8}$$

At considerable distance from the point S, the motion is represented approximately by Newton's equation

$$V^2=\frac{2m}{r}, \tag{9}$$

where m is the mass at S. Comparing (7), (8) and (9) we see that $C=2m$, and so

$$\gamma=1-\frac{2m}{r}. \tag{10}$$

It is interesting to note that the velocity measured by the moving observer always has the value

$$V^2=\frac{2m}{r},$$

as in Newton's theory.

5. **Value of** ds. Consider events occurring in a plane through S. Let O, P be points at distance r from S and let $d\phi$ be the angle OSP as measured by the falling observer. Since this observer makes measurements as in restricted relativity,

$$arc\ OP=r\,d\phi.$$

I assume that this is also the distance OP measured by the fixed observer.

In the plane OSP, the Minkowski interval ds between two events is given by

$$ds^2=dT^2-r^2d\phi^2-dR^2.$$

Replacing dR and dT by their values from (5), this becomes

$$ds^2=\gamma dt^2-r^2d\phi^2-\frac{1}{\gamma}dr^2, \tag{11}$$

We have found that two radii appear to the fixed observer at O to converge to a point at distance γr from O. If the observer is at the point $r=2m$,

$$\gamma r=\left(1-\frac{2m}{2m}\right)r=0.$$

Hence to the fixed observer the sun is not the point $r=0$ but the point $r=2m$. This is also indicated by the expression for ds^2. For when $\gamma=0$, dr must be zero if ds is to be finite. No measurement beyond $\gamma=0$ exists.

6. **Motion of a free particle.** By the equivalence hypothesis the motion of the falling observer should neutralize evidences of gravitation in his immediate neighborhood. Thus a free particle which instantaneously coincides with the falling observer G should appear to be free from gravitation and so to be moving in a straight line with constant velocity. If a plane is passed through S and the initial direction of motion of the free particle, its acceleration is in this plane. Hence the particle should continue to move in this plane.

As seen by G the motion of the free particle at each point of its path should satisfy the condition

$$\delta\int ds=\delta\int\sqrt{dT^2-r^2d\phi^2-dR^2}=0.$$

Hence, the path should be one for which the integral

$$\int ds=\int\sqrt{\gamma dt^2-r^2d\phi^2-\frac{1}{\gamma}\,dr^2}$$

has a stationary value. Let

$$L=\sqrt{\gamma\left(\frac{dt}{ds}\right)^2-r^2\left(\frac{d\phi}{ds}\right)^2-\frac{1}{\gamma}\left(\frac{dr}{ds}\right)^2}$$

$$=\sqrt{\gamma\left(\dot{t}\right)^2-r^2\left(\dot{\phi}\right)^2-\frac{1}{\gamma}\left(\dot{r}\right)^2}.$$

Then the condition to be satisfied is

$$\delta\int L\,ds=0.$$

Differentiating and replacing h by 1, the Euler conditions

$$\frac{d}{ds}\left(\frac{\partial L}{\partial \dot{t}}\right)-\frac{\partial L}{\partial t}=0,$$

$$\frac{d}{ds}\left(\frac{\partial L}{\partial \dot{\phi}}\right)=\frac{\partial L}{\partial \phi}=0,$$

give

$$\gamma\frac{dt}{ds}=C, \qquad r^2\frac{d\phi}{ds}=h, \tag{12}$$

where C and h are constants. As a third equation we use the identical relation

$$ds^2=\gamma dt^2-r^2d\phi^2-\frac{1}{\gamma}dr^2. \tag{13}$$

By solving the differential equations (12) and (13) we can determine the motion of the particle.

7. **Particle falling from rest.** In this case $h=0$. Let dT, dR be values measured by the observer falling with the particle. The equations expressing measurements dt, dr of the fixed observer, in terms of dT, dR, have the form

$$dt=A\,dT+B\,dR,$$

$$dr=E\,dT+F\,dR. \tag{14}$$

At a point in the moving system $dR=0$ and $dT=ds$. Hence, from (12) and (14),

$$A=\frac{dt}{dT}=\frac{dt}{ds}=\frac{C}{\gamma},$$

$$E=\frac{dr}{dT}=\frac{dr}{ds}=\sqrt{C^2-\gamma},$$

the last expression being obtained by substituting

$$dt=\frac{Cds}{\gamma}$$

in (13) with $d\phi=0$. Using these values of A and E and substituting in the general equation

$$ds^2=dT^2-dR^2=\gamma dt^2-\frac{1}{\gamma}dr^2,$$

we then find

$$F=C, \quad B=-\frac{1}{\gamma}\sqrt{C^2-\gamma}.$$

Hence equations (14) become

$$\begin{aligned} dt&=\frac{C}{\gamma}dT-\frac{1}{\gamma}\sqrt{C^2-\gamma}\,dR, \\ dr&=CdR-\sqrt{C^2-\gamma}\,dT. \end{aligned} \tag{15}$$

Solving for dT and dR, we get

$$\begin{aligned} dT&=Cdt+\frac{1}{\gamma}\sqrt{C^2-\gamma}\,dr, \\ dR&=\frac{C}{\gamma}dr+\sqrt{C^2-\gamma}\,dt. \end{aligned} \tag{16}$$

In case of a particle falling from infinity, $C=1$ and equations (15), (16) reduce to (5), (6).

In the measurement of a fixed distance ($dT=0$), from (15),

$$dr=C\,dR.$$

In the measurement of time at a fixed point ($dr=0$), from (16),

$$dT=C\,dt.$$

These measurements made by the two observers have a constant ratio. They are equal only in the case $C=1$ when the moving observer falls from infinity.

The velocity of the falling observer ($dR=0$) as seen by the fixed one is

$$\frac{dr}{dt}=-\frac{\gamma\sqrt{C^2-\gamma}}{C}.$$

This is zero when $C=\sqrt{\gamma}$ and so the motion starts from the point where

$$C^2=\gamma=1-\frac{2m}{r}.$$

At this point equations (16) become

$$dT=Cdt=\sqrt{\gamma}\,dt,$$

$$dR=\frac{C}{\gamma}dr=\frac{1}{\sqrt{\gamma}}dr. \tag{17}$$

Although both observers are here at rest they do not obtain the same measurements. This shows the effect of gravitation on measurements of length and time. The falling observer may be considered to measure correctly. The fixed observer in a gravitational field obtains measurements of time increased in the ratio

$$\frac{1}{\sqrt{\gamma}}$$

and of radial distance diminished in the ratio

$$\sqrt{\gamma}.$$

The factors $\sqrt{\gamma}$ in the expression

$$ds^2=\left(\sqrt{\gamma}dt\right)^2-r^2d\phi^2-\left(\frac{dr}{\sqrt{\gamma}}\right)^2$$

have the effect of changing the gravitational measures dr, dt into Galilean measures.

8. **Measurement of time at a fixed point.** Let dT, dR be measurements made by the free observer at O who is accelerated but has zero velocity. Let w be the velocity, as seen by this observer, of a free particle passing through O. For this particle, using (17), we find

$$ds^2=dT^2-R^2d\phi^2-dR^2=(1-w^2)dT^2=(1-w^2)\gamma dt^2,$$

whence, from (12),

$$1-w^2=\frac{1}{\gamma}\left(\frac{ds}{dt}\right)^2=\frac{\gamma}{C^2}. \tag{18}$$

If the observer on the passing particle makes a measurement of time at the point O of the system instantaneously at rest, since both systems are Galilean, he will find w to be the velocity of that system and so

$$(1-w^2)dT'^2=dT^2=\gamma dt^2. \tag{19}$$

Comparing (18) and (19), we see that

$$dT'=C\ dt.$$

Hence an observer on a free particle finds measurements of time at fixed points that have a constant ratio to those of the gravitational observers at those points.

9. **Orbit of a planet.**[2] Eliminating ds and dt from equations (12) and (13), we get

$$\left(\frac{h}{r^2}\frac{dr}{d\phi}\right)^2+\frac{h^2}{r^2}=C^2-1+\frac{2m}{r}+\frac{2mh^2}{r^3}.$$

Writing $u=\frac{1}{r}$, this becomes

$$\left(\frac{du}{d\phi}\right)^2=\frac{C^2-1}{h^2}+\frac{2mu}{h^2}+2mu^3-u^2. \tag{20}$$

Let $u_1<u_2<u_3$ be the roots of the cubic

$$2mu^3-u^2+\frac{2mu}{h^2}+\frac{C^2-1}{h^2}=0.$$

Then

$$u_1+u_2+u_3=\frac{1}{2m}, \tag{21}$$

$$u_1u_2+u_2u_3+u_3u_1=\frac{1}{h^2}. \tag{22}$$

The method used by Eddington and others, in which approximations have been made in the differential equations, has been criticised. The following treatment is here given to meet these criticisms.

In case of the sun,

$$m = 1.47 \text{ km.},$$

and for the planets u is of the order

$$10^{-8} \text{ km.}$$

At aphelion and perihelion $\dfrac{du}{d\phi}$ is zero. Hence u passes through two of the roots in description of the orbit. These roots, u_1 and u_2 are then of the order 10^{-8} km., and from (21) u_3 is about one hundred million times larger than either of these.

We can write (20) in the form

$$\left(\frac{du}{d\phi}\right)^2 = 2m(u-u_1)(u-u_2)(u-u_3)$$

whence

$$\phi = 2\int_{u_1}^{u_2} \frac{du}{\sqrt{2m(u-u_1)(u_2-u)(u_3-u)}} \tag{23}$$

is the angle turned through in a complete description of the orbit. Taking out a factor u_3 and expanding in series, this becomes

$$\phi = \frac{2}{\sqrt{2mu_3}} \int_{u_1}^{u_2} \frac{du}{\sqrt{(u-u_1)(u_2-u)\left(1-\dfrac{u}{u_3}\right)}}$$

$$= \frac{2}{\sqrt{2mu_3}} \int_{u_1}^{u_2} \frac{du}{\sqrt{(u-u_1)(u_2-u)}} \left(1+\frac{1}{2}\frac{u}{u_3}+\cdots\right)$$

$$= \frac{1}{\sqrt{2mu_3}} \left[2\pi + \frac{\pi}{2}\frac{u_1+u_2}{u_3} + \cdots\right].$$

Using

$$u_3 = \frac{1}{2m} - (u_1+u_2),$$

by a further expansion we obtain

$$\phi = 2\pi\left[1+\frac{3}{2}m(u_1+u_2)+\ldots\right],$$

the neglected terms in each case being of the order

$$\left(\frac{u_1+u_2}{u_3}\right)^2.$$

Dividing (22) by (21), we have to the same order of approximation

$$u_1+u_2=\frac{2m}{h^2},$$

whence

$$\phi = 2\pi\left[1+\frac{3m^2}{h^2}+\ldots\right]. \tag{24}$$

In a complete description of the orbit, the perihelion advances the fraction

$$\frac{3m^2}{h^2}$$

of a revolution approximately, the approximation being of the order of 1 part in 10^8.

10. **Deflection of a ray of light.** In case of a ray of light,

$$ds=0.$$

The equations

$$\gamma\frac{dt}{ds}=C, \qquad r^2\frac{d\phi}{ds}=h$$

show that C and h are infinite. The ratio

$$\frac{C}{h}=\frac{\gamma dt}{r^2 d\phi}=k \tag{25}$$

is, however, in general finite. Substituting these values in (20) we have

$$\left(\frac{du}{d\phi}\right)^2=k^2+2mu^3-u^2 \tag{26}$$

to determine the path of a ray of light.

Suppose the nearest approach to the sun is

$$r=\frac{1}{u}=a.$$

At that point

$$\left(\frac{du}{d\phi}\right)^2=k^2+\frac{2m}{a^3}-\frac{1}{a^2}=0.$$

Subtracting from (26), we have

$$\left(\frac{du}{d\phi}\right)^2=2m\left(u^3-\frac{1}{a^3}\right)-\left(u^2-\frac{1}{a^2}\right).$$

In a complete description of the path from infinity back to infinity, the total change of direction is

$$\phi=2\int_0^{\frac{1}{a}}\frac{du}{\sqrt{\frac{1}{a^2}-u^2-m\left(\frac{1}{a^3}-u^3\right)}}$$

$$=2\int_0^{\frac{1}{a}}\frac{du}{\sqrt{\left(\frac{1}{a^2}-u^2\right)\left(1-2m\dfrac{\frac{1}{a^2}+\frac{u}{a}+u^2}{\frac{1}{a}+u}\right)}}$$

$$=2\int_0^{\frac{1}{a}}\frac{du}{\sqrt{\frac{1}{a^2}-u^2}}\left(1+m\frac{\frac{1}{a^2}+\frac{u}{a}+u^2}{\frac{1}{a}+u}+\dots\right)$$

$$=\pi+4\frac{m}{a}$$

approximately. In case of a ray passing close to the sun the neglected terms are of the order

$$\left(2m\frac{\frac{1}{a^2}+\frac{u}{a}+u^2}{\frac{1}{a}+u}\right)^2<\left(3\frac{m}{R}\right)^2<\left(\frac{1}{150{,}000}\right)^2$$

11. **Path of light near the center of the sun.** Suppose the sun concentrated within a radius less than $3m$. The expression

$$\left(\frac{du}{d\phi}\right)^2 = k^2 + 2mu^3 - u^2$$

has a minimum value at

$$u = \frac{1}{3m}, \qquad r = 3m.$$

If, then, a ray of light penetrates beyond

$$r = 3m,$$

$\frac{du}{d\phi}$ can never become zero and so it can never recede. It will continue to penetrate inward. The equation

$$r^2 \frac{d\phi}{dt} = \gamma \frac{h}{C}$$

shows that an infinite time will be required to reach the position

$$\gamma = 0, \qquad r = 2m.$$

If the ray is inclined so as just to reach $r = 3m$,

$$k^2 + 2m\left(\frac{1}{3m}\right)^3 - \left(\frac{1}{3m}\right)^2 = 0,$$

and so

$$\left(\frac{du}{d\phi}\right)^2 = \left(u - \frac{1}{3m}\right)^2 \left(2mu + \frac{1}{3}\right).$$

The total angle turned through in reaching $r = 3m$ is

$$\phi = \int_0^{\frac{1}{3m}} \frac{du}{\left(\frac{1}{3m} - u\right)\sqrt{2mu + \frac{1}{3}}} = \infty.$$

The ray will describe a spiral of an infinite number of terms and require an infinite time to reach $r = 3m$.

If the ray is directed along the circle $r = 3m$, $\frac{du}{d\phi}$ will remain zero, the ray describing a circular orbit.

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 147.)

THE EQUATION OF STATE FOR METHANE GAS PHASE*

By Frederick G. Keyes, Leighton B. Smith and David B. Joubert

The isotherms for gaseous methane have been measured by Amagat.[1] The absolute volumes are not given, but merely the volumes relative to the capacity of a certain manometric tube. The data extend from 14.7° to 100.1° and over a pressure range of 40 to 300 atms. Aside from the relative pressure-volume products of Amagat there are no data from which the constants of the equation of state for the gas phase can be evaluated. Moreover, the question of purity is of importance, and Amagat at the time (1880) did not have the facilities for insuring the purity of a hydrocarbon such as methane. In the present investigation the attempt has been made to measure the isometrics of methane between 0° and 200° and over a pressure range from about 36 to 300 atms.

There are advantages experimental and theoretical in choosing the "isometric method" of investigating the pressure-volume-temperature relation for a fluid. Of the three quantities the volume is the most difficult to measure and control and in the attempt to keep the volume constant attention is particularly focused upon the conditions necessary accurately to maintain a chosen volume. The theoretical work in connection with the equation of state[2,3,4,5,6] has made it seem highly probable that in

* This work is published by permission of the Director of the Bureau of Mines. The present paper together with the other papers of this number are some of the investigations required by the Bureau of Mines in perfecting the processes for the extraction of helium from natural gas.

This investigation was undertaken by the Massachusetts Institute of Technology at the request of the Bureau of Mines, working in coöperation with the War and Navy Departments. The Bureau of Mines as well as the Massachusetts Institute of Technology contributed liberally in funds needed to carry forward the work. The funds of the Bureau of Mines were allotted from Army and Navy appropriations made available for research work connected with extracting helium from natural gas.

1 Amagat, Annales de Chimie et de Physique **22**, 367, 1881.
2 Phillips, Jour. of Math. and Phy. M. I. T. **1**, 42, 1921.
3 Phillips, Proc. Nat. Acad. Sci. **7**, 172, 1921.
4 Keyes, Jour. Amer. Chem. Soc. **43**, 1452, 1921.
5 Keyes, Jour. of Math. and Phy. M. I. T. **1**, 89, 1922.
6 Keyes, Proc. Nat. Acad. Sci. **3**, 323, 1917.

the case of a fluid composed of molecules of invariable type, the pressure should vary linearly with the temperature at constant volume. The attempt to test this linearity of pressure increase directly makes it further desirable to employ the isometric method. In fact, the investigation of the sources of error in the methods used to carry out measurements at constant volume has led by successive approximations to considerable improvements in the apparatus. The relatively simple form of the equation of state for a fluid composed of invariable molecular species requiring the pressure to be linear in the pressure-temperature relation makes it, moreover, comparatively easy to determine the constants of the equation of state.

In the investigation here presented it was hoped to improve materially the accuracy with which a given volume could be maintained and reproduced. The pressure measurements also have been improved from the point of view of accuracy and sensitiveness. The temperature measurements made by means of the platinum resistance thermometer were found at the conclusion of the measurements not to be as reliable as was at first thought. This circumstance was due to defects in the resistance bridge which, however, after having been discovered, proved not to invalidate the temperatures by more than probably 0.1° at most. Of course temperatures are desired on the absolute temperature scale, and the comparisons of the platinum thermometer with the gas scale leave uncertainties at present which may amount to 0.1° at 200°.

The present data on methane are the most nearly linear of any pressure-temperature data thus far examined and verify the particular form of the equation of state. Considerable improvement in the apparatus doubtless can be realized in future work, however, and a still more accurate test made of this most important relation.

Preparation of Pure Methane

The methane was prepared by heating a mixture of dry sodium acetate and soda-lime. The diagram, Fig. 1, illustrates the apparatus employed for generating and purifying the gas. The dry powdered sodium acetate and soda-lime were contained in

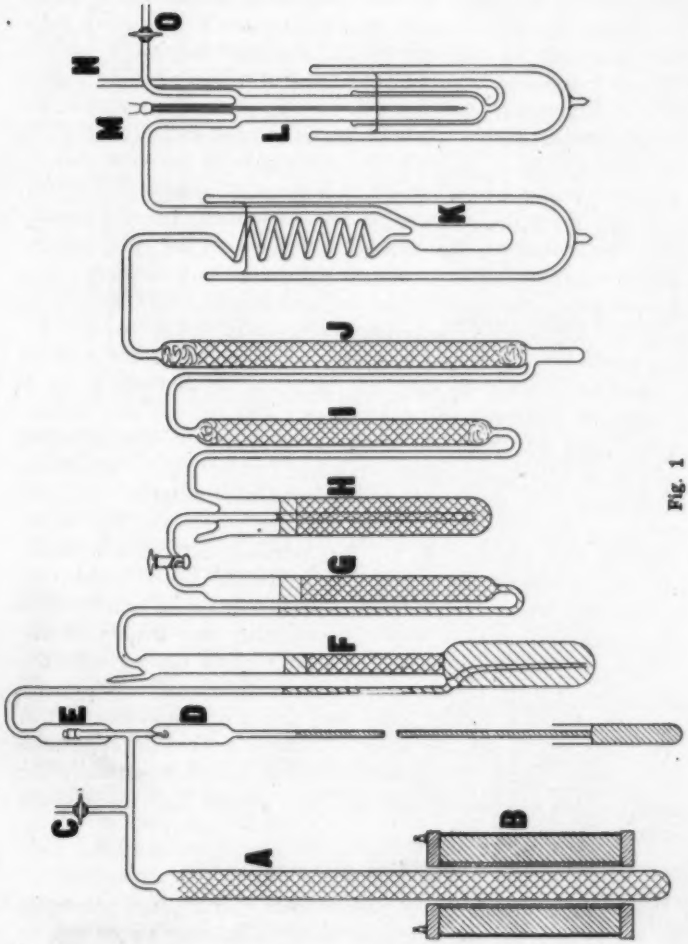


Fig. 1

the pyrex tube A about 2.5 cm. in diameter and 50 cm. in length. The salt mixture could be heated regularly and the gas evolution controlled by the movable electric furnace B. A safety valve was provided by the barometric mercury column D, while a Bunsen type valve, consisting of a band of rubber covering a small hole in the glass reëntrant portion at E, prevented surges in the liquid purifying tubes. Evacuation of the salt mixture tube was secured through C, while F contained 20 per cent fuming sulphuric acid employed to retain acetone or unsaturated hydrocarbons. Quite a proportion of acetone is formed in the acetate soda-lime reaction. The tube G contained 98 per cent concentrated sulphuric acid to absorb SO_3 fumes and H 20 per cent caustic soda solution followed by solid caustic I for the removal of CO_2. The tube J containing P_2O_5 served finally to dry the gas which was condensed by means of liquid air in the receiver K, whence it could be distilled back and forth from K to L to remove hydrogen and other gases. The tube L was double-walled and silvered, but arranged so that the double-walled portion could be exhausted or made conducting by admitting hydrogen. The thermocouple M sufficed to observe the constancy of melting of the solid methane within L. The frozen methane was pumped at O. The purified material was finally allowed to expand through O into a five-liter globe which previously had been exhausted hot to remove adsorbed moisture and other gases. A special analysis apparatus was a part of the system and will be presented in a later paper dealing with the isometrics of nitrogen-methane mixtures. The analytical apparatus indicated that foreign gases were not in excess of one part in 500, which was the limit of accuracy attainable from the apparatus at the time. From the precautions taken in the preparation the purity of the methane would have been greater than the analysis indicated.

The Pressure Gauge

The gauge was similar in construction to the gauge employed by Keyes and Brownlee[7] except that the floating piston was of about 1 cm. diameter. Improvement has been made in the

7 Keyes and Brownlee, Jour. Am. Chem. Soc. **40**, 25, 1918.

TABLE I

Calibration of the Pressure-Measuring Piston

Mean Temp. of Column	*Total Corr. Weight Grams*	*Height in mm.*	*Corr. for Oil Level*	*Corr. for Tape Length*	*Mm. at 0°*	*Constant of Piston mm./g.*	*Per Cent Dev. from Mean Value 1.0255*
19.30	8490.85	8826.0	−85.1	.....	8708.3	1.02560	+0.010
19.07	8464.75	8798.5	−85.1	+0.9	8682.4	1.02575	+0.024
18.66	8287.67	8613.5	−85.1	+0.7	8498.4	1.02543	−0.007
18.66	7487.30	7790.0	−85.1	+0.1	7677.2	1.02536	−0.014
18.32	7036.82	7327.5	−85.1	+0.4	7217.2	1.02562	+0.012
19.13	6685.74	6968.0	−85.1	+0.1	6857.7	1.02557	+0.020
19.36	6208.53	6475.0	−85.1	+0.1	6366.2	1.02540	−0.010
19.19	6043.33	6305.0	−85.1	+0.1	6197.0	1.02544	−0.006
19.23	5572.50	5820.5	−85.1	+0.1	5714.2	1.02543	−0.007
19.49	4759.30	4984.0	−85.1	−0.1	4880.6	1.02547	−0.003
18.85	4413.13	4627.5	−85.1	−0.2	4525.8	1.02553	+0.003
18.85	3464.68	3650.0	−85.1	.....	3552.0	1.02520	−0.024

Mean Value of Constant 1.0255 mm. per gram.

mercury column used to calibrate the gauge. This consists in using a platinum needle for electrical contact at the surface of the mercury in the short arm of the column to facilitate detecting the equilibrium of the column. Better temperature control of the column was also secured by enclosing it in a channel-shaped support closed on the open face by adjustable pieces of cardboard. The equilibrium of the piston was determined by the use of a telephone using an audion bulb as shown in diagram Fig. 2. This device enabled a very feeble current to be used at the surface of the mercury, avoiding emulsification of the oil, which seems to take place when the secondary of an induction coil is used to indicate contact of the mercury with the needle. The emulsification is of very great importance in making compressibility measurements with the apparatus of Fig. 2, since emulsification of the mercury and oil amounts to removing a small quantity of mercury from the piezometer portion of the system.

The length of the mercury column was measured on a steel tape stretched by a load of seven kilos. The calibration of the tape was effected under the same stretching load by comparison with a standard meter compared at the United States Bureau of Standards. Table I gives a summary of the data from which it

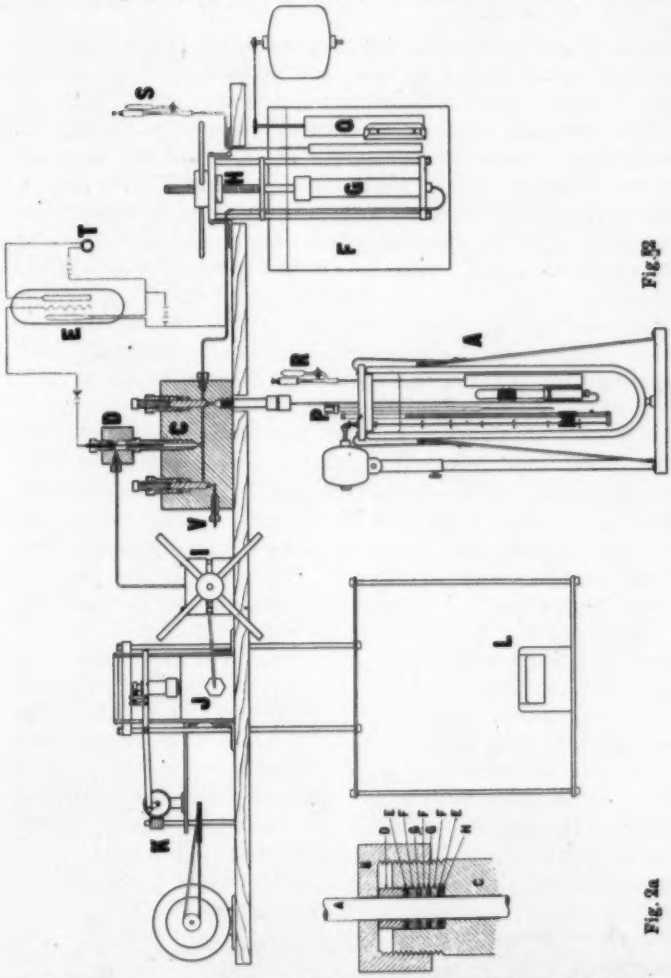
will be seen that the maximum deviation from the mean is about one part in four thousand, while the average deviation is about one part in eight thousand.

The Compressibility Apparatus and Method of Loading the Piezometer

The general apparatus is shown in Fig. 2, which is a further development of the apparatus used by Keyes and Felsing[8]. The floating pressure piston with scale pan and motor for oscillating the piston is represented at J, L, and K. The oil injector I serves to adjust the height of the floating piston and to compensate for leak of oil around the floating piston. The steel block C contains a stopcock V for exhausting and a mercury-level-indicating insulated needle D. This contact serves to detect equilibrium of the load on the piston and the pressure exerted by the material in the piezometer. For example, if too great a weight is on the piston the mercury will be depressed and if too small a weight it will rise and make contact. One gram suffices, as a rule, to make or break the contact. A shut-off is provided for closing the piezometer B from the entire apparatus while connection is made from the block C to the mercury volume-displacement piston apparatus G submerged in a constant temperature bath F, whose contents are stirred by means of the motor and propeller apparatus Q. The nut H serves to force the piston into the mercury, driving it through fine steel tubing into the piezometer. The advance of the piston is indicated by one hundred divisions engraved on the under portion of the nut. Whole turns are counted by a " cyclometer " not shown in the drawing. It is possible with the 16 mm. piston driven by a 7.1 threads per cm. screw to estimate 0.001 turn of the nut corresponding to about 0.00028 c.c. The packing of the piston which moves into the cylinder G consists of cotton fabric heated in ceresin wax to 160°, and hard rubber forced into place by means of a steel ring driven by a screw cap.* The packing is perfectly tight over long

[8] Jour. Am. Chem. Soc. **41**, 589 1919.

* The diagram, Fig. 2a, shows the method of applying the packing to the piston in the mercury volume injector. The piston is represented by A and the nut driving the packing at B through pressure on the steel ring D. At the bottom of the packing gland is a steel ring H which also is a snug fit to the piston. E, E indicates hard rubber rings and F, F, F the cotton fabric (such as unbleached cotton) impregnated quickly with ceresin wax at



160°. G, G are rings of soft steel. The annular width of the packing gland is about 3 mm. and the depth for moderate pressures (500 atms.) about 3 to 4 cm. The hard rubber ring protects the waxed packing from the kerosene of the bath and serves to wipe the piston as it moves backward and forward, thus minimizing the removal of wax. This latter objective is not as satisfactorily accomplished as desirable, but no better method of wiping the piston has been applied.

periods of use after having been seasoned by exposing it to several hundred atmospheres with successive tightenings of the driving nut. A similar packing is used on the stopcocks of the block C.

The constant temperature bath represented at A, Fig. 2, consists of a pyrex Dewar tube 6.6 cm. in inside diameter and 40 cm. in length. The disposition of the platinum thermometer, stirrer, heater and mercury in the steel regulator is evident from the figure. For the bath fluid a high boiling light oil sufficed for the range 50° to 200°, while an ice bath served to maintain the piezometer at 0°. The cover of the bath is of asbestos wood and carries the bearing for the stirrer and binding posts for the electrical connections of the heater. The Dewar tube bath here represented is very convenient and has been employed to 330°. It possesses obvious advantages due to its permitting a view of the interior at all times and the heat insulation is excellent. The Dewar tube, however, requires prolonged heating at 450° during exhaustion. Recent tubes silvered in such a manner as to leave a clear strip 2 cm. to 5 cm. in width parallel to the long axis have greater heat-insulating properties, at the same time permitting a view of the interior. The silver will not peel off once it has been slowly and thoroughly baked out during exhaustion.

The piezometer is represented in detail at A, Fig. 3. It was made in one piece from cold rolled steel, the lower end being spun shut and welded with the oxy-acetylene flame. A left-hand thread was cut on the outer portion, where it screwed into the top piece E surrounded by a cooling coil of copper B. The latter piece carried a screw driver F passing through a packing gland and sealed with mercury. The piezometer was locked by means of the plug D, which had a 0.75 mm. hole drilled throughout its length. The locking of the piezometer was secured by the compression of the gold washer C against a seat in the piezometer by means of the screw D. The purpose of the cooling coil about E was to preserve the packing gland during the exhaustion of the bomb at 350°.

Methane is, of course, above its critical temperature at ordinary temperatures, and it was necessary to place in the piezometer sufficient methane to give a range of volumes per gram from 8 c.c. to 35 c.c. over the temperature range 0° to 200°. The capacity

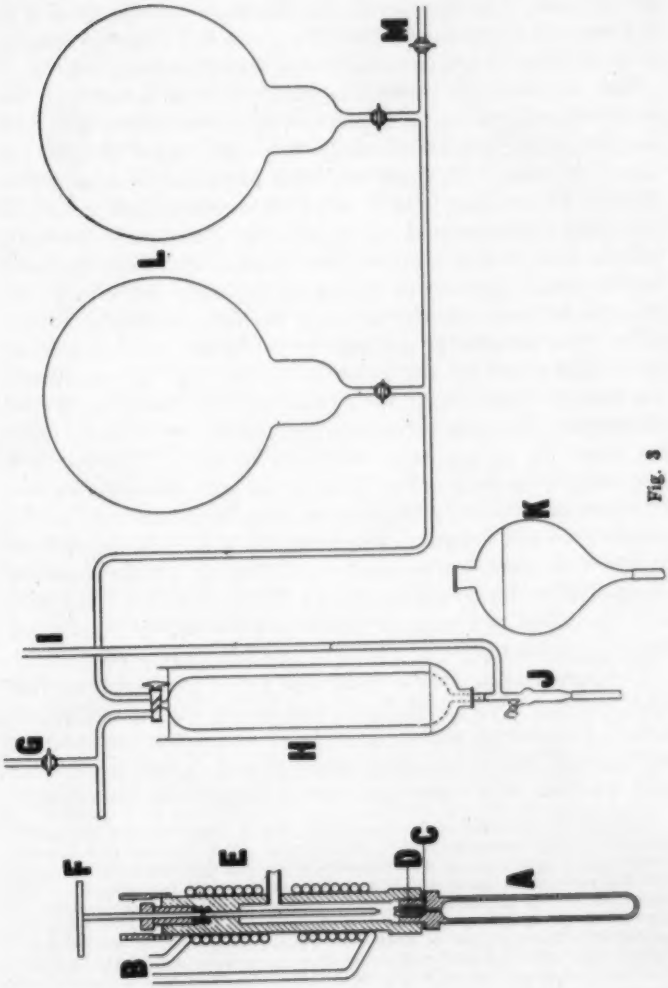


FIG. 3

of the piezometer was 7.6574 c.c. at zero to the under surface of the gold disk. The quantity of methane employed was about 0.17 to 0.19 g., corresponding to about 260 c.c. at N.T.P. and producing about 40 atms. in the piezometer at ordinary temperatures.

The procedure of loading consisted in first exhausting the burette H, connected by means of the two-way stopcock with the piezometer; the latter being, of course, heated to drive off adsorbed matter. Methane was then permitted to expand into H from the holders L and, when temperature equilibrium had been established, the pressure was read on the mercury column I. The burrette was of the constant volume type, with the lower burette mark engraved on a tube of the same diameter as the manometric tube, thereby avoiding capillary depression corrections. The quantity of methane in the burette was transferred to the piezometer by cooling the latter in liquid air and raising the mercury reservoir K, thus liquifying the methane in the piezometer. The piezometer was then locked by screwing down the screw D by means of the screw driver F. The methane remaining in the leads and in E above the gold disk was removed by means of a Toepler pump and the volume measured at a known temperature and pressure. To obtain the true mass requires the equation of state for methane or it suffices for the accuracy obtainable* to employ the weight of a liter at N.T.P. The weight of a liter taken as a mean of nine determinations by Baume and Perrot[9] is 0.7168 gram or 1394.2 c.c. N.T.P. per gram.

The loaded piezometer is connected with a piece of hexagonal steel carrying a 0.75 mm. bore steel tubing locking against an annealed aluminum washer, and placed inverted in the constant temperature bath. Referring again to Fig. 2, the piezometer with its steel tube can then be connected with the block C

* The gas is measured in the burette H, Fig. 3, under other conditions of temperature and pressure than N. T. P., under which the liter is measured. Strictly, one should know the compressibility and coefficient of expansion of the gas to obtain the true weight of the actually measured quantity. The use of the perfect gas laws using the measured weight per liter leads to no appreciable error, however, in the case of methane, as was proved when the constants of the equation of state were obtained. It will be shown in the present paper that the weight of a liter of methane calculated by the equation of state agrees very well with the experimental determination of Baume and Perrot.

[9] Baume and Perrot, Jour. Chim. Phys. **7**, 1371, 1909.

and the steel lead exhausted through V to the gold washer serving to confine the methane in the piezometer. After closing the stopcock in block C at V, mercury can be run in by screwing in the piston of the mercury volume injector G. It is to be added that a plug replaced the oil lead from I in D during the exhaustion and the oil lead was replaced after filling the block and lead with mercury. The oil lead having been connected, mercury is brought to the needle point* by manipulating the oil injector I and volume injector G. By this means a zero setting can be obtained at a definite pressure corresponding to the position of the mercury which is in contact with the gold disk closing the piezometer. After the zero setting is obtained the pressure is increased to several hundred atmospheres and in about twenty-four hours the gold disk, weakened by amalgamation with the mercury, is punctured, bringing the mercury into contact with the methane. By means of the mercury injector G a setting can be made for a chosen specific volume of methane and a series of pressures and temperatures observed.

It is necessary to know the temperature dilation of the mercury as well as its compressibility† while the stretch of the steel piezometer and apparatus can be obtained by separate blank measurements. For the true expansivity with temperature of the steel piezometer, the data of the Reichsanstalt were correlated as a function of the temperature as follows:

* One of the difficulties encountered in the test series of measurements was the emulsification of the mercury at the needle point and junction of oil and mercury. This has the effect of making the contact uncertain and is due to the use of too high a voltage. It was to remedy this defect that the audion bulb system represented at E and T was introduced.

† The compressibility of mercury is a function of both pressure and temperature. Thus Bridgman gives the compressibility at one atmosphere as 3.80×10^{-6} at 0° and 3.95×10^{-6} at 22°. The decrease of the compressibility with pressure is given as about three per cent for the first thousand atmospheres. The effect of pressure increase may be neglected in the present work since 400 atmospheres were not exceeded. The temperature effect on the stretch of the piezometer is determined as the sum of that due to the compressibility of the mercury contained in the piezometer and the stretch of the piezometer itself. These direct measurements failed to disclose any pronounced effect on the combined mercury compressibility and piezometer stretch because of the small amount of mercury (7.6 c.c.) contained in the piezometer and the smallness of the temperature coefficient of stretch of the piezometer. The value 3.9×10^{-6} was assumed for the mercury compressibility independent of the temperature. The total stretch of the piezometer amounted to 4.4×10^{-6} c.c. per atm.

$$V_t^{Pt} = V_0(1+3.25\times10^{-5}t+2.85\times10^{-9}t^2-1.65\times10^{-11}t^3).$$

The equation for the volume of mercury as a function of the temperature as given by Callendar and Moss was employed.

$$V_t^{Hg} = V_0(1+1.80555\times10^{-4}t+1.2444\times10^{-8}t^2+2.539\times10^{-11}t^3)$$

TABLE II

Observed Pressure Represented as a Linear Function of the Temperature at Constant Volume.

Volume	0°	50°	100°	150°	200°	
			p = 0.16160T − 7.714			
35.104	36.37	44.55	52.63	60.70	68.66	Pressure obs.
	36.43	44.51	52.59	60.67	68.75	Pressure calc.
			p = 0.19148T − 10.389			
30.089	41.89	51.55	61.17	70.68	80.09	Pressure obs.
	41.91	51.49	61.06	70.63	80.21	Pressure calc.
			p = 0.23520T − 14.809			
25.075	49.21	61.20	72.96	84.64	96.22	Pressure obs.
	49.38	61.13	72.88	84.63	96.38	Pressure calc.
			p = 0.30412T − 23.081			
20.059	59.85	75.35	90.56	105.63	120.42	Pressure obs.
	59.99	75.19	90.40	105.60	120.81	Pressure calc.
			p = 0.42860T − 40.398			
15.045	76.47	98.34	119.88	140.95	161.76	Pressure obs.
	76.67	98.10	119.53	140.96	162.39	Pressure calc.
			p = 0.71429T − 87.629			
10.030	107.25	143.66	179.61	214.59	250.03	Pressure obs.
	107.47	143.19	178.90	214.62	250.33	Pressure calc.
			p = 0.81880T − 105.812			
9.026	117.08	159.21	200.51	240.62	280.55	Pressure obs.
	117.84	158.78	199.72	240.67	281.60	Pressure calc.
			p = 0.96295T − 132.575			
8.024	129.73	179.03	227.58	275.10	321.92	Pressure obs.
	130.45	178.60	226.70	274.89	323.04	Pressure calc.

The shifting of the temperature requires, for preserving constancy of the methane volume, a resetting of the mercury injector G to compensate for the combined increase in volume of the mercury in the piezometer and the dilation of the piezometer with temperature and pressure. The method of making this computation, knowing the stretch of the piezometer and apparatus with pressure and the dilation of the piezometer and mercury with temperature, is obvious.

The Experimental Data

The data were taken first at 50° continuing to 100°, 150° and 200°, making the observations, at zero, last in a Dewar tube filled with ice. In Table II will be found the absolute temperatures and pressures for the fixed volumes beginning with about 35 c.c. per gram of methane. A linear equation is given with each volume which has been used to calculate the pressures recorded under each observed pressure. It will be noted that the first and last observations are slightly higher than the observed values. This was finally traced to a slight but gradual drift in the compressibility of the packing of the stopcocks in the block C and that used to pack the piston in the mercury injector G. For this reason in making up the linear equation more weight was attached to the three middle sets of data at each specific volume.

The equation of state gives, for the tangent of the pressure-temperature lines at constant volume, the expression $\frac{R}{v-\delta}$. The magnitude of R per mol is known with tolerable accuracy[10] being $82.058 \frac{c.c., atm.}{degrees\ C., mol.}$. The molecular weight of methane has been

TABLE III

Values of δ Observed and Calculated by the Equation

$$\log_{10} \delta = 0.56195 - \frac{1.05}{v}\ ;\ \delta = 3.647e^{-\frac{2.42}{v}}$$

Spec. Vol.	$\left(\frac{R}{v-\delta}\right)^{obs.}$	δ *obs.*	$\left(\frac{R}{v-\delta}\right)$ *cal.*	δ *calc.*
35.104	0.16160	3.438	0.16143	3.404
30.089	0.19148	3.365	0.19149	3.366
25.074	0.23520	3.318	0.23514	3.312
20.059	0.30412	3.233	0.30413	3.233
15.045	0.42860	3.106	0.42861	3.106
10.030	0.71429	2.866	0.71418	2.866
9.026	0.81880	2.777	0.82054	2.790
8.024	0.96295	2.710	0.96099	2.699

[10] Keyes, Jour. Am. Soc. Refrig. Eng. **8**, 505 1922.

TABLE IV

Cohesive Pressure Term deduced for each Temperature from the Pressure-Temperature Tangent compared with the Cohesive Pressure calculated by means of Equation.

$$\phi = \frac{9802.2}{(v+0.565)^2}$$

Volume	ϕ 0°	ϕ 50°	ϕ 100°	ϕ 150°	ϕ 200°	*mean* ϕ	*calc.* ϕ
35.104	7.77	7.67	7.67	7.68	7.80	7.72	7.70
30.089	10.41	10.33	10.28	10.34	10.51	10.38	10.43
25.075	15.03	14.80	14.80	14.89	15.07	14.92	14.91
20.059	23.22	22.92	22.92	23.05	23.47	23.12	23.00
15.045	40.60	40.16	40.05	40.41	41.03	40.45	40.23
10.030	87.86	87.15	86.92	87.65	87.93	87.50	87.33
9.026	106.56	105.38	105.02	105.85	106.86	105.94	106.56
8.024	133.29	132.14	131.74	132.36	133.69	132.64	132.89

TABLE V

Isometrics of Methane used to determine the Constants of the Equation of State. Pressures compared with those calculated by Equation of State.

$$p^{\text{atm.}} = \frac{5.1173}{v-\delta}T - \frac{9802.2}{(v+0.565)^2}; \quad \log_{10}\delta = 0.56195 - \frac{1.05}{v}.$$

Volume c.c./g	0°	50°	100°	150°	200°	
35.104	36.37	44.55	52.63	60.70	68.66	Pressure obs.
	36.39	44.46	52.53	60.60	68.67	Pressure calc.
30.089	41.89	51.55	61.17	70.68	80.09	Pressure obs.
	41.87	51.45	61.02	70.59	80.17	Pressure calc.
25.074	49.21	61.20	72.96	84.64	96.22	Pressure obs.
	49.31	61.07	72.83	84.59	96.34	Pressure calc.
20.059	59.85	75.35	90.56	105.63	120.42	Pressure obs.
	60.07	75.28	90.48	105.70	120.90	Pressure calc.
15.045	76.47	98.34	119.88	140.95	161.76	Pressure obs.
	76.80	98.27	119.70	141.13	162.56	Pressure calc.
10.030	107.25	143.66	179.61	214.59	150.03	Pressure obs.
	107.74	143.45	179.16	214.86	150.57	Pressure calc.
9.026	117.08	159.21	200.51	240.62	280.55	Pressure obs.
	117.56	158.59	199.61	240.64	281.67	Pressure calc.
8.024	129.73	179.03	227.58	275.10	321.92	Pressure obs.
	129.59	177.64	225.69	273.74	321.79	Pressure calc.

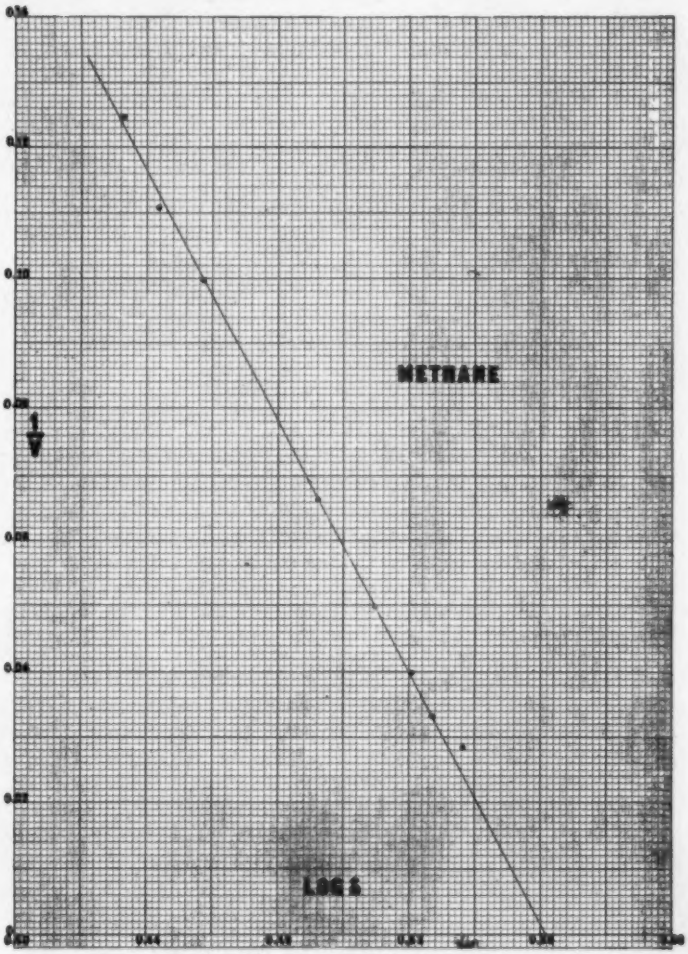


Fig. 4

taken as 16.035, using the atomic weights $H=1.0075$ and $C=12.005$. The value of R per gram of methane is therefore 5.1173.

The values of δ may be calculated using the relation $\delta = v - \frac{R}{\left(\frac{\partial p}{\partial T}\right)_v}$, and since $\delta = \beta e^{-a/v}$ a plot can be prepared, using as coördinates $\log \delta$ and $\frac{1}{v}$. The plot is reproduced in Fig. 4, showing that methane follows the function $\delta = \beta e^{-a/v}$. In Table III are listed the volumes per gram, the tangent obtained directly from the isometrics, the values of δ calculated from the tangents, the calculated tangents and δ values calculated by means of the δ equation accompanying the table.

To complete the equation of state it is necessary to obtain the constants of the cohesive pressure term $\phi = \frac{A}{(v+l)^2}$. For this purpose the values of the constants of the linear equations given in Table II may be used or the calculated tangent of each pressure-temperature datum may be used to deduce a corresponding ϕ value. For each volume this gives with the data of Table II five values of ϕ numerically identical except for errors in observation. Table IV gives, corresponding to each temperature, the value of ϕ obtained from the experimentally determined slope. The mean of these values is then calculated over to $\frac{1}{\sqrt{\phi}}$, which gives a straight line when plotted with v, as represented in Fig. 5. The equation heading the table has been used to compute ϕ "calculated." It is evident that the ϕ function represents the experimental data as well as could be expected. The complete equation of state for methane is, therefore:

$$p = \frac{5.1173}{v-\delta}T - \frac{9802.2}{(v+0.565)^2} \qquad (1)$$

$$\log_{10} \delta = 0.56195 - \frac{1.05}{v}$$

In Table V will be found the pressures calculated by means of equation (1) for comparison with the observed pressures.

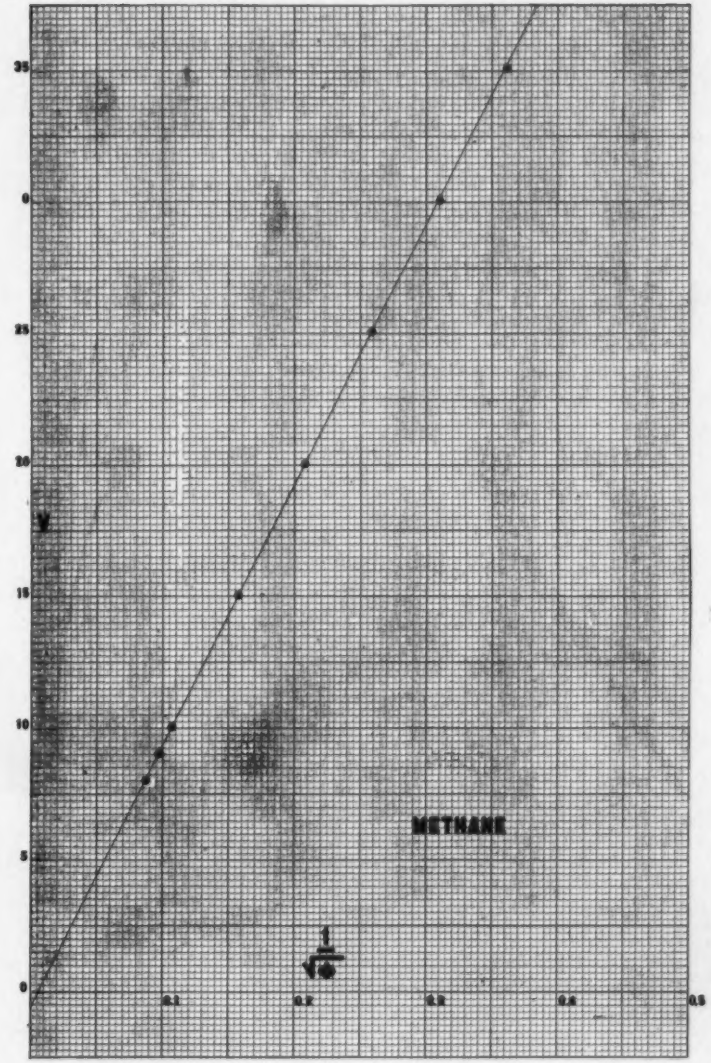


Fig. 5

This series of measurements, used to evaluate the constants of the equation of state, was made after studying the defects in the apparatus and introducing the amplifier circuit represented at D, E, T in Fig. 1. An earlier series obtained before the introduction of the latter is presented in Table Va, showing the disturbing effect of the emulsification of the mercury, due to the high voltage of the induction coil secondary used to excite the telephone on contact of the mercury with the needle point.

TABLE Va

Series of Methane Isometrics obtained before Improved Mercury Contact Detector was employed. Pressures compared with those calculated by Equation of State.

$$p = \frac{5.1173}{v-\delta}T - \frac{9802.2}{(v+0.565)^3}\,;\quad \log_{10}\delta = 0.56195 - \frac{1.05}{v}$$

Volume c.c./g	0°	50°	100°	150°	200°	
37.394	34.35	42.00	49.51	56.98	64.49	Pressure obs.
	34.34	41.87	49.40	56.94	64.47	Pressure calc.
32.053	39.51	48.54	57.49	66.28	75.13	Pressure obs.
	39.53	48.55	57.37	66.30	75.22	Pressure calc.
26.710	46.56	57.71	68.59	79.30	90.17	Pressure obs.
	46.61	57.55	68.49	79.44	90.38	Pressure calc.
21.368	56.67	71.06	85.07	98.85	112.88	Pressure obs.
	56.80	70.93	85.06	99.18	113.31	Pressure calc.
16.026	72.63	92.74	112.41	131.55	151.19	Pressure obs.
	72.83	92.69	112.54	132.39	152.24	Pressure calc.
10.684	101.67	135.43	167.60	199.04	231.19	Pressure obs.
	102.31	135.22	168.13	201.04	233.95	Pressure calc.
9.615	110.76	149.42	186.22	222.24	258.90	Pressure obs.
	111.60	149.35	187.09	224.83	262.58	Pressure calc.
8.547	122.56	167.80	209.65	252.37	295.33	Pressure obs.
	123.06	167.19	211.33	255.47	299.61	Pressure calc.

The results of Amagat's measurements on the compressibility of methane are presented in the form of relative pressure volume products. By means of the equation of state, however, the ratio of the relative volume to the volume per gram may be found for one temperature and pressure. This factor will then serve as a means of comparing the Amagat observations with the present

measurements or the equation of state. In Table VI, therefore, the volume corresponding to 39.5 atms. and 14.7° is 34.4 c.c./g., giving a factor of 1.899 relative volume units corresponding to 1 unit of c.c./g. The volumes at 131.6 and 263.2 atms. for 14.7° and 100° are computed using this factor, affording a basis for comparison with the volumes calculated by means of the equation of state at corresponding temperatures and pressures. Below 130 atms. the agreement is good, but Amagat's volumes are progressively larger as higher pressures are approached.

TABLE VI

Comparisons of the Relative Volumes given by Amagat with the Volumes calculated at Corresponding Pressures and Temperatures by means of the Methane Equation of State.

Pressure	Temperature		
Atm.	14.7	100.1	
39.5	34.4 $\frac{\text{c.c.}}{\text{g.}}$		Amagat
	34.4 $\frac{\text{c.c.}}{\text{g.}}$		Computed
131.6	8.10	13.7	Amagat
	8.91	13.7	Computed
263.2	4.85	7.13	Amagat
	4.00	6.95	Computed

Weight of a Liter of Methane at N.T.P.

Baume has most recently measured the normal density of methane[11]. A total of eleven determinations were made of which two were discarded in taking the mean. The extreme variation is 0.166 per cent in the nine values accepted, which give a mean of 0.7168 gram per liter N.T.P. Moissan and Chavanne[12] have also published a density, but only two determinations were made and conditions were not favorable for very exact work. The values relative to air are 0.5540 and 0.5554, showing a difference of 0.25 per cent.

[11] Baume, Jour. de Chim. Phys. **7**, 369, 1909.
[12] Moissan and Chavanne, C. r. **140**, 407, 1905.

The equation of state leads to the value 0.71718 gram per liter, which is one part in 1900 greater than 0.7168 obtained by Baume.

The coefficients of expansion at constant volume and constant pressure for one atmosphere have been published by Leduc[13]. The constant volume value is 0.003679 as compared with 0.0036796 by the equation of state. The constant pressure coefficient given by Leduc is 0.003681, while that computed is 0.0036834.

SUMMARY

1. A new apparatus has been described for measuring the pressure-volume-temperature properties of a fluid by the "isometric" method. The particular piezometer employed is especially adapted for work with gases whose critical temperature lies well below zero.

2. The isometrics of methane have been measured and found to be linear within the limits of experimental error between zero and two hundred degrees up to three hundred atmospheres.

3. The equation of state has been found to represent the pressure-volume-temperature relation accurately. The following equation is for the units atm., c.c./g., degrees centigrade absolute.

typ. error

$$p=\frac{4.1175}{v-\delta}T-\frac{9802}{(v+0.565)^2}$$

$$\log_{10}\delta=0.56195-\frac{1.05}{v}.$$

4. The weight of a liter of methane calculated by means of the equation of state is 0.71718 as compared with 0.7168 given by Baume by direct measurement. The difference of one part in about nineteen hundred is well within the limits of experimental error of the Baume measurements.

5. The coefficients of temperature expansion at one atmosphere obtained from the equation of state are in agreement with the estimates independently made by Leduc.

[13] Leduc, C. r. **148**, 1173, 1908.

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 148.)

THE THERMODYNAMIC PROPERTIES OF METHANE

By Frederick G. Keyes, Robert S. Taylor and Leighton B. Smith

1. **Introduction. The Vapor Pressure of Methane.** There are very few published data for the vapor pressure of liquid methane. Olszewski's[1] results extend from the critical temperature to the freezing point, but the pressures are several atmospheres greater than the recent measurements of Cardoso[2] in the interval $-84.4°$ to $-97.0°$. The critical pressure, for example, obtained by Olszewski is 54.9 atms. at a critical temperature given as $-81.8°$ whereas Cardoso gives 45.60 atms. at $-82.85°$. No other measurements have been found in the literature.

In the case of methane there are two very material difficulties connected with securing accurate vapor pressure values. Thus it is necessary to maintain and measure temperatures from $-80°$ to $-180°$ and insure that the temperature readings lie on the absolute scale of temperature. The latter objective is by no means easy to insure, since the comparisons of secondary standard thermometers with the gas scale have not reached a stage where satisfactory concordance has been attained between various investigators. The relation of the platinum resistance thermometer to the gas scale, for example, has been shown by Henning[3] not to be the same below zero as above zero where the Callendar formula applies. In fact, no two of Henning's eight platinum resistance thermometers appeared to give identical readings at all temperatures below zero, although the δ constants of Callendar, obtained by using 0°, 100°, and 419.4° for some of the thermometers, were almost identical. The general inference was that the differences between the gas scale and the Callendar formula temperatures of the platinum resistance thermometers were very markedly affected by small variations in the temperature coefficient of the platinum wire.

[1] Olszewski, C. r. **100,** 940, 1885.
[2] Cardoso, Jour. de Chim. et Phys. **13,** 332, 1915.
[3] Henning, Ann. d. Phys. **40,** 635, 1913.

The further need in accurate low temperature work is a constant temperature bath whose temperature can be changed at will from zero to the lowest temperatures required. The use of liquids boiling under constant pressure for this purpose has been highly developed in the Leiden cryogenic laboratory of Professor Onnes, but is not as convenient as desirable owing to the necessity of changing the bath liquids for studies covering long temperature ranges. It is, in addition, necessary to vary and maintain constant the pressure over the boiling liquids. The device used by Henning in the paper referred to above consisted of a test tube, submerged in a bath of petroleum ether, into which liquid air is dropped as required. Evidently a bath of this description would be troublesome to use where observations are to be made requiring concentration of attention on the details of the physical measurements.

The purity of the methane to be used is of paramount importance. For the present work samples of the methane were employed prepared as described in the preceding paper on the equation of state of methane.

In view of the uncertain status of the behavior of the platinum resistance thermometer at low temperatures an investigation had already been made in the physics department laboratories of this Institute of the relation between the scales of the platinum resistance thermometers actually used in the present investigations with the gas scale. The freezing points of a number of substances lying between zero and the boiling point of oxygen were also measured in terms of the constant volume hydrogen gas scale to serve as calibration temperatures.

The question of the thermodynamic scale is of particular importance at low temperatures, since the effect of a given error in temperature measurements is of increasing significance as lower temperatures are approached. Thus for example, 0.1° at the ice point, 273.14, is an error somewhat greater than 1 per 3,000, whereas 0.1° at the boiling point of oxygen, 90.20, is of more than three times this magnitude. The temperatures recorded in the present paper are, then, those obtained by means of a platinum resistance thermometer compared directly with the constant volume hydrogen thermometer at a number of temperatures between zero and the normal boiling point of oxygen.

2. **Apparatus Details.** The apparatus of first importance is the cryostat represented to scale in Fig. 1. It consists of two pyrex Dewar tubes, one of which A serves to contain liquid air, or, under certain conditions, liquid ammonia. Support for the larger tube is provided by means of a brass ring encircling the flask and attached thereto are three brass strips screwed to the cast-iron

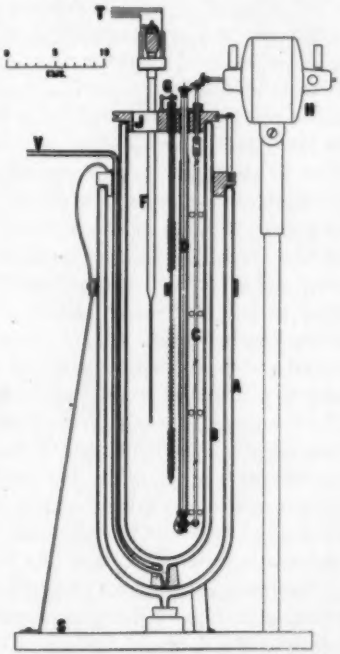


Fig. 1

base S. The cast-iron base also serves to carry the support rod for the motor H used to stir the contents of the bath itself. The inner Dewar tube is supported in the larger tube by means of an asbestos wood cover into which the smaller tube is cemented. The inner Dewar tube is provided with a cork support at its tip, from which a tube V leads to a source of hydrogen or to a vacuum.

The outer tube is silvered except for a rectangular strip which permits a view of the interior. The inner Dewar tube is supplied with a cover which serves as a support for the stirrer, heater, temperature regulator and platinum resistance thermometer. The cover of hard rubber is held firmly in place by three bolts carrying tongues of brass which fit into a slot turned into the periphery of the hard rubber cover. An opening is also provided at J for the introduction of the apparatus upon whose contents observations are to be made. It is, of course, essential that the introduction of heat by conduction should be a minimum and for this reason the stirrer rod C is interrupted by a hard rubber connector just under the cover. The shank of the thermometer is of monel metal turned to about 0.2 mm. thickness, and having the silver sheath containing the platinum wire silver-soldered thereto. The regulator consists of a 3 mm. width and 0.75 mm. thickness invar-brass thermostat metal.* This is wound in a helix as indicated and the upper end soldered to a thin brass tube. The lower end carries, floating, a fine monel rod passing loosely through a hard rubber bushing shown shaded at G. Here two platinum contacts are arranged and as the helix winds and unwinds, due to temperature changes, contact is made and broken. The sensitivity is limited by the pressure necessary to make electrical contact. The maximum sensitiveness which has thus far been attained at the lower temperatures is about 0.1°. The platinum resistance thermometer, however, indicating 0.001° makes it easy to secure a temperature constant to 0.01°. The combination of hand regulation with the automatic requires an operator to watch the galvanometer of the resistance bridge and manipulate resistances in accordance with the deflections of the galvanometer. The bimetallic helix, on the other hand, would have great sensitivity were it not for the really considerable pressure needed for good electrical contact. It is hoped that in time means for surmounting the latter difficulty will be evolved, since it is most convenient to have the bath automatically regulated.

The heater consists of a very thin steel, or preferably monel, tube upon which is wound the resistance wire over thin mica.

* This excellent material was obtained in several thicknesses and lengths through the kindness of the H. A. Wilson Co. of Newark, N. J.

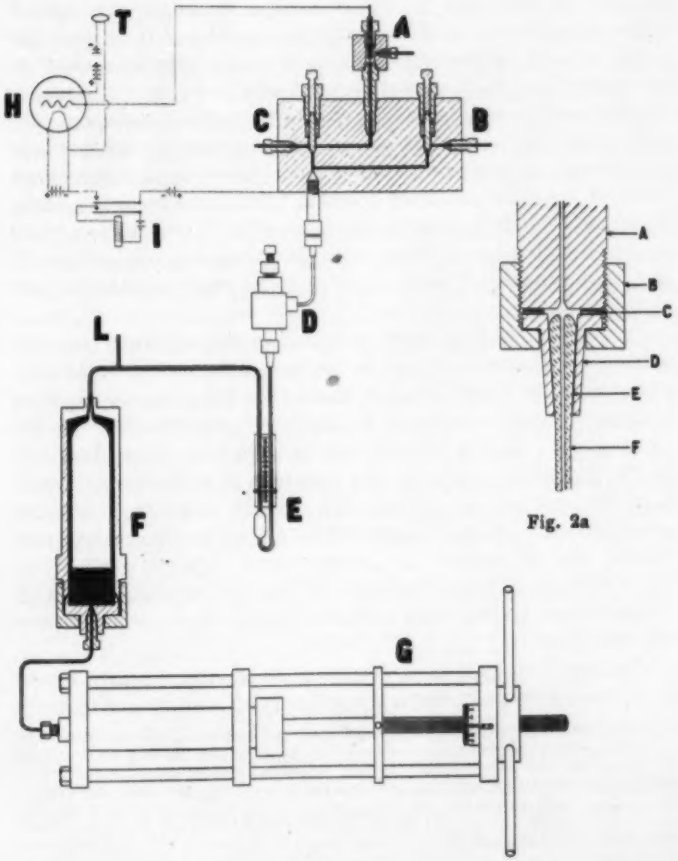


Fig. 2

Fig. 2a

Talc plugs serve to insulate the free end of the wire which passes through the center of the supporting tube.

The method of operating the bath consists in adjusting the pressure of hydrogen in the interspace of the Dewar tube B until sufficient cooling of the bath fluid is secured to balance the mean value of the heating current. For the lowest temperatures, for example, as good as possible conductivity of the interspace is required and a centimeter pressure of hydrogen is sufficient. At high temperatures, on the other hand, a relatively low pressure is necessary on account of the greater difference in temperature between the contents of the cryostat bath B and the surrounding liquid air. For temperatures above $-30°$ it is best to use liquid ammonia in the outer dewar tube, and thus any temperature in the range between $0°$ and $-180°$ may be easily established and maintained.

The vapor pressures were measured in two separate pieces of apparatus. Pressures above several atmospheres were measured at the time the densities of the liquid were being measured, while a special apparatus was used for the lower pressures down to the triple point. In Fig. 2 is represented the block C as described in the preceding paper on the equation of state for methane. A is the mercury oil contact, the oil lead connecting with the piston pressure gauge. C leads to the mercury volume-measuring injector and B leads to the vacuum pump. The electrical circuit for indicating mercury contact at the oil junction within A consists of an audion bulb, induction coil primary, dry batteries and telephone.

The steel stopcock D serves to shut off the mercury in the pyrex glass volume-measuring apparatus* E, which connects by

* The coefficient of temperature expansion of pyrex glass has not been measured at low temperatures. The following equation for the true volume at any temperature t is based on the mean expansion measurements in a weight-thermometer of pyrex glass between 0 and 100, and 100 and 218°.

$$V_t^{\text{pyrex glass}} = V_0(1+9.68\times10^{-6}t+3.11\times10^{-9}t^2)$$

The error that extrapolation to $-180°$ may introduce in the measurements of the specific volume of liquid methane is inconsiderable unless the coefficient of expansion of pyrex glass is widely different from soda glass in its general expansion behavior. This is not inferred since its expansion properties are quite similar to soda and other glasses above zero.

The expansion of the volumenometer with pressure was determined at zero degrees by blank measurements with the bell F sealed off from the

0.75 mm. bore pyrex glass tubing at one side with the steel cock** D and at the other with the pyrex glass bell (2.75 cm. diameter and 12.5 cm. long) enclosed in the steel case F. The capillary lead L is used to exhaust the glass portion previous to the introduction of the methane. The compressor G connecting with F serves to force methane into E where the liquid volumes were measured. It is perceived that the apparatus consists of a constant volume portion E, which can be filled with liquid methane at any temperature in the liquid region by manipulating the mercury injector G transferring methane from the reservoir F at ordinary temperatures.

The volume of E (1.5798 c.c. at 0°) together with the capillary leads was determined by filling with mercury and weighing. The volume of the bell within F (about 75 c.c.) was measured by means of the piston G. The injector G (total volume capacity 56 c.c.) was calibrated by weighing the mercury ejected for each five turns of the nut advancing the piston. The position of the piston was indicated by a "cyclometer" giving the number of whole turns, and the fractions of a turn, on the nut whose periphery was divided into one hundred divisions. The piston was so adjusted that practically at its maximum inward travel the mercury stood at a mark on the capillary of determined volume per unit length above F. The glass bell was, of course, so

volumenometer. Correction could, therefore, be made for the stretch of E with pressure although this was not determined as a function of the temperature. Previous experience with soda glass above zero has shown that the temperature coefficient of the pressure stretch is very small within the elastic limits of the glass.

**In Fig. 2a is represented an enlarged drawing of the method employed to connect the steel and glass. The glass capillary F is thickened to an inverted cone shape and ground to fit the steel piece D. The member D is then warmed and a thin layer of a cement made from shellac which has been digested on a water-bath with fifteen per cent of North Carolina oil of tar, is wiped over the ground surface. The glass member is now seated in the steel part D, turning the glass member in its seating position until the cement is squeezed out and the ground surfaces in as close contact as possible. Connection can now be made with any other part of the steel apparatus, as represented at A, by means of a union B, using an annealed aluminum disk C. The glass capillary F should be joined *in situ* to the remaining portion of the glass apparatus to avoid strains at the rigid steel construction. The joint of the steel and glass bell F is made in the same manner as described. The joints described are vacuum tight, resist the action of mercury and hold against pressure to the limit of the glass. They cannot be used, however, above 100°.

proportioned (75 c.c. capacity) that when the piston was withdrawn to the complete outward travel of the screw, mercury sealed the lower end of the bell. Methane from the storage globe was now passed over into a measuring burette, similar to the one used in loading the piezometer employed in measuring the isometrics of the gas phase, and condensed finally in E at the temperature of liquid oxygen. The capillary lead at L was then sealed and the gas remaining in the leads between L and the measuring burette pumped off and measured. Before E was allowed to warm to room temperature the mercury was lowered in F to the maximum by withdrawing the piston of G. The methane could then be safely allowed to evaporate from E, filling a space of about 56 c.c. and producing a total pressure of only 10 atms. at ordinary temperatures.

To make a measurement of the specific volume the volumenometer E was brought into the cryostat already described. A glass scale divided into millimeters was placed back of the volumenometer serving to give indication of the position of the level of the meniscus of liquid methane relative to two etched marks on the capillary extensions from the volumenometer bulb. At a fixed temperature mercury was forced over from a second mercury injector communicating from B until the meniscus was just about at the level of the cover of the cryostat and fixed in position by closing the steel stopcock D. By means of G methane was forced to condense in E until the liquid methane menisci were about at the two etched marks on the volumenometer stems. A fixed volume of liquid methane was, therefore, confined by the gas phase present in the capillary leads. The total mass of methane was known after sealing at L and the volume, temperature and pressure of the methane existing in the gas phase, from the reading of the position of the piston of the injector G and the volume of the glass capillary tubing. By means of the equation of state the mass of this known total gaseous volume could be computed, and the mass of the liquid methane of known volume in E deduced. Before changing the temperature of the cryostat the steel cock D could be opened and an observation made of the vapor pressure. In this manner practically the whole temperature range of the existence of the liquid phase could be measured. The critical temperature was ascertained and also the critical pressure.

In the procedure described no mention has been made of the influence of adsorption in removing methane from the phase under observation. The volumenometer E was exhausted at 360° for several hours previous to admitting the methane. No certainty is afforded that adsorption did not take place, but freeing the glass surface from adsorbed moisture appears, from general experience, to minimize the adsorption of the permanent gases.* The bell F could not be evacuated hot, so that no certain knowledge is available as to the amount of methane adsorbed. The total

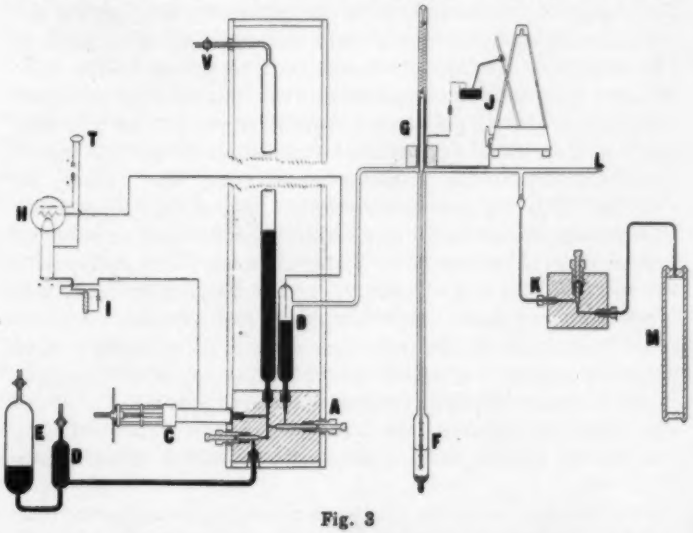


Fig. 3

mass of methane was, however, sufficiently large, so that, if ten molecular layers of methane were adsorbed, the effect would scarcely be detectable with the accuracy attainable in the volumenometer measurements.

The measurements of saturation pressure below several atmos-

* It was shown by Eumorphopoulos (Proc. Roy. Sci. **90** A, 189, 1914) that only by repeatedly heating and rinsing with dry nitrogen could the coefficient of volume increase with temperature at constant pressure be made reproducible. Isometric measurements with ammonia in this laboratory have indicated that adsorption is greatly minimized by long baking out of the glass at the best vacuum obtainable.

pheres were carried out in a special apparatus, since the piston gauge is not suitable for low-pressure measurements. The general apparatus is represented in Fig. 3. The manometer tubes were selected of uniform bore, 1.5 cm. in outside diameter and the actual diameter along the length determined by weighing mercury taken from successive intervals along the length of the longer leg. The short leg of the manometer was provided with a finely pointed platinum wire sealed into the closed end and the diameter accurately determined at the section in the plane of the point. With the true tube diameters a table was then computed giving the correction for capillary depression for different heights of mercury. The corrections for capillary depression with tubing 1.5 cm. I.D. will rarely exceed a few hundredths mm. with tubes of moderate uniformity of bore. Each manometer tube was ground to a seat in the steel block A* having steel cocks to cut off the two legs of the manometer and the levelling reservoir E. The mercury in the reservoir E was passed through the trap D to prevent air from gaining access to the manometer tubes, and all connections were of glass. Compressed air and vacuum served to manipulate the entrance and exit of mercury to the manometer, while fine adjustment was secured by means of the mercury piston injector C. The purpose of the platinum contact B in the short arm was to aid in observing equilibrium of the methane in the container F and to save continually reading the mercury level in the short arm, since the reading of the level when contact just makes is reproducible to the limit of sensitiveness of the cathetometer (0.02 mm.).

The methane container during the actual measurements consisted of the tube F containing an electro-magnetically operated glass stirrer as indicated. The coil G was energized periodically by means of the metronome contacting device represented. It

* The ground joints and block were warmed and set with the shellac cement, as described in the case of the steel-glass joint represented in Fig. 2. An enlarged and threaded portion was produced in the steel block above the ground cone, for the purpose of preventing the tubes floating off their seat. The tubes themselves were enlarged, as indicated, at a point where they would come within the threaded part and at the time of seating the tubes, when both glass and steel were hot, cement was poured into the threaded cavity. With the construction here indicated the glass cones can be made and ground so that the bore of the glass coincides with the communicating hole in the steel, eliminating thereby any tendency to trap gas.

is, of course, necessary to adjust the period of the metronome to the elastic characteristics of the spring by which the stirrer is suspended. The soft iron rod constituting the armature is enclosed in glass just below the eye used to fasten the lower end of the spring.

The exhaustion of the apparatus took place through the lead at L, while the long leg of the manometer was exhausted or exposed to the atmosphere at V depending on the magnitude of the pressure to be measured. The methane to be used in the measurements was transferred from the glass storage globes to the steel tube container M provided with a steel block carrying a cock and lead K. Methane was condensed in M by means of liquid air, after having been thoroughly exhausted. Connection was made to the glass apparatus by means of the shellac cement. When the entire apparatus was thoroughly exhausted to the cock in the steel block K, the tube F was brought into the cryostat, adjusted to the lowest temperature ($-180°$), and by opening the cock of the steel methane container, a quantity of methane was condensed in F for the measurement of the vapor pressure. The exhausting lead L carried a stopcock in order to permit of pumping the methane between successive measurements, thus insuring the absence of foreign gas, although the methane during its introduction into the container M was treated to remove all permanent gases. At the conclusion of a day's measurements, the methane could be transferred from the tube F to the container M and held under pressure for future measurements.

3. **The Temperature Measurements.** The temperatures recorded should lie on the absolute or thermodynamic scale and, while numerous investigations have resulted in fixing with considerable certainty the thermodynamic scale above zero, the temperature scale below zero, as already stated, is by no means as completely investigated. The difficulties, indeed, are increased in the region below zero, due to the difficulties of refrigeration, lack of convenient cryostats and errors introduced in the gas thermometry by adsorptive effects. The latter are of increasing significance as the temperature is lowered and are, moreover, par-

ticularly difficult to investigate quantitatively. Unfortunately, as Henning has shown, the platinum resistance thermometer does not follow the Callendar formula in its relation to the thermodynamic scale below zero. Moreover, owing to the fact that the wire contracts on cooling, it is not easy to devise a method of winding which will avoid the production of strains. Above zero, on the other hand, the wire expands and the tension of the wire on its support is relieved.

Owing to the importance of an accurate knowledge of the true temperature indications of the particular platinum thermometer employed in the present work, an extended comparison was made directly with the constant volume hydrogen thermometer employed in an investigation of the low temperature scale by Keyes, Townshend and Young in this Institute. The actual curve, (Fig. 14 of their paper), shows the difference between the Callendar formula platinum resistance thermometer temperatures and those of the quartz hydrogen thermometer of constant volume. The hydrogen gas scale temperature of the boiling point of pure oxygen at 76 cm. was found to be -182.94 as compared with -182.93 of Onnes[4] and -182.97 of Henning.[5] The boiling point of carbon dioxide at 76 cm. was similarly found to be -78.53 as compared with -78.52 found by Henning.[5]

4. **The Vapor Pressure Measurements.** The measurements at higher pressures made in the apparatus represented in Fig. 2 extend from about 4.5 atms. at 133.6° abs. to the critical temperature 191.03°. The low pressure measurements extend from about 7.5 degrees above the triple point[6] temperature to about 114.6°.

The higher pressure measurements consist of two series presented in Table I. The low pressures were measured in a small cryostat whose diameter (6.7 cm.) was small compared with the length (30 cm.). Efficiency of stirring of the bath fluid of propane and butane is necessary before the experimental tube can be assumed to be at the same temperature as the thermometer.

[4] Onnes and Braak, Leiden Comm. No. 107a, 1908.
[5] Henning, Ann. d. Phy. **43**, 289, 1914.
[6] Crommelin, Com. Leiden Phys. Lab. No. 131, 1912. The temperature of the triple point is given as -183.15 and the pressure 7.0 cm.

TABLE I

Methane Vapor Pressures

	Series 1			*Series 2*	
Temperature Abs.	*Observed Pressure Atms.*	*Calc. Pressure Atms.*	*Temperature Abs.*	*Observed Pressure Atms.*	*Calc. Pressure Atms.*
133.628	4.514	4.493	143.380	7.574	7.515
138.558	5.874	5.880	158.549	14.634	14.839
143.495	7.590	7.558	168.267	21.737	21.637
148.439	9.579	9.565	168.351	21.707	21.704
153.385	11.949	11.936	172.355	25.004	25.073
158.339	14.639	14.711	178.189	30.500	30.626
163.295	17.897	17.928	181.203	33.684	33.812
172.437	25.146	25.146	186.084	39.626	39.449
178.189	30.486	30.626	186.147	39.389	39.525
181.203	33.700	33.812	188.005	41.807	41.835
186.147	39.511	39.525	189.931	44.207	44.326
			191.031 Crit.	46.063	45.792

TABLE II

Low Vapor Pressure Measurements of Methane

T	*Series 1 Pressures Atms.*	*Series 2*	*Series 3*	*Series 4*	*Series 5*	*Series 6*	*Mean of Series 4, 5, 6*	*Pressure Calc. by Equation*
97.293	0.2638	0.2625	0.2620	0.2575	0.2575	0.2571	0.2574	0.2574
100.902	0.3855	0.3847	0.3815	0.3774	0.3785	0.3781	0.3780	0.3780
106.003	0.6276	0.6271	0.6228	0.6216	0.6210	0.6197	0.6208	0.6196
110.023	0.8925	0.8928	0.8858	0.8839	0.8852	0.8829	0.8840	0.8830
114.631	1.2917	1.2903	1.2860	1.2846		1.2812	1.2829	1.2823

Table II gives the low pressure series. The resistance bridge, in each series of measurements, made at different times, was brought to the same indication and the bath regulated at the corresponding temperature. In this manner the various changes in the external conditions affecting the measurements could be investigated. It was found necessary to increase the speed of the stirring of the bath markedly to secure constancy of the vapor pressure and also the agitation of the liquid methane by means of the electro-magnetic stirrer. To establish the absence of hydro-

gen or air the vapor phase of the methane could be pumped off from time to time during the measurements, and at the conclusion of the day's run from the frozen methane in the steel container before closing the steel cock K. The three final series 4, 5, and 6 show equilibrium was attained and these values have been used to form the mean pressure upon which the equation for the vapor pressure as a function of the temperature was based.

Some disappointment was felt that the measurements at higher pressures presented in Table 1 were not more concordant. This is not due to any lack of sensitiveness in the pressure-measuring device or lack of constancy in the temperature of the cryostat. It is believed to be due possibly to lack of sufficient stirring or agitation of the liquid methane under measurement. The construction of the apparatus and the purpose it had to serve precluded an effective stirring device, but a form of stirrer is being perfected which may permit the full utilization of the sensitiveness of the present pressure-measuring apparatus.

The equation used to relate the pressure to the temperature is of the form employed for ammonia and carbon dioxide.

$$\log p = -\frac{a}{T} + m + bT + cT^2 + dT^3 + \ldots \qquad (1)$$

The evaluation of the constants of this equation can sometimes, as was illustrated in the case of ammonia and carbon-dioxide, be best attained by using the equation in the "critical-constants" form:[7]

$$\log p = -\frac{Z(T_c - T)^2 + \omega}{T} + m \qquad (2)$$

In the case of methane, however, it was found to be preferable to select the approximate equation $\log p = -\frac{a'}{T} + m'$ and, by comparing the calculated with the observed logarithms of the pressures, obtain values designated as

$$\Delta \log p = \log p \text{ obs.} - \log p \text{ calc.}$$

These values were then plotted with the reciprocal of the cor-

[7] Thermodynamic Properties of Ammonia. Keyes and Brownlee, Wiley & Sons, page 10, 1916.

responding absolute temperatures and the best curve drawn to represent the final relation. The curve was then represented by means of the equation.

$$\Delta \log p = -\frac{\Delta a}{T} + \Delta m + bT + cT^2 + dT^3 \ .$$

where Δa and Δm are constants which can be used in comparing with the approximate equation to give the final equation for $\log p$ as a function of the absolute temperature. The final equation is as follows where $T = (t + 273.13)$

$$\log_{10} p^{\text{atm.}} = -\frac{595.546}{T} + 8.09938 - 4.04175 \times 10^{-2} T + 1.68655 \times 10^{-4} T^2 - 2.51715 \times 10^{-7} T^3 \qquad (3)$$

TABLE III

Methane Vapor Pressure Data

Temperature Deg. Abs.	*Vapor Pressure Calc. Atms.*	*Temperature Deg. Abs.*	*Vapor Pressure Calc. Atms.*	*Temperature Deg. Abs.*	*Vapor Pressure Calc. Atms.*
95.00	0.1982	125.00	2.670	160.00	15.74
100.00	0.3444	130.00	3.641	165.00	19.14
105.00	0.5646	135.00	4.853	170.00	23.05
110.00	0.8813	140.00	6.338	175.00	27.49
111.52	1.0000	145.00	8.132	180.00	32.51
115.00	1.319	150.00	10.27	185.00	38.15
120.00	1.905	155.00	12.79	190.00	44.42
				191.03 Crit.	45.79

In Table III will be found the vapor pressures in atmospheres for each five degrees beginning with 95° abs. and ending with the critical pressure. The critical temperature and pressure were directly observed and may be compared with the value given by Cardoso* of $-82.°85$, as compared with $-82.°10$ obtained in the present investigation.

Cardoso worked under great difficulties in connection with his thermometry and exercised the greatest care and skill in the construction of his pentane thermometers. Difficulties were encountered also in connection with the lag in the expansion and

* Cardoso, Jour. de Chim. Phys. **13**, 332, 1915.

contraction of the glass comprising the thermometers, so that in spite of all the precautions taken errors of temperature were difficult to avoid.

In Table IV will be found the pressures given by Cardoso at the temperature observed with his pentane thermometer. The pressure measurements were made with a closed manometer, using the usual precautions to insure accuracy. It will be noted in the table that the Cardoso pressures are uniformly higher than those calculated by the Equation (3) and that the differences in temperature corresponding thereto are roughly the same order of magnitude, except the datum at 176.14°. The average temperature difference amounts to 0.56° and this correction applied to Cardoso's temperatures would bring the corresponding pressures into fair accord with the present measurements.* It will be noted in the

TABLE IV
Cardoso Vapor Pressure Data

T	188.74	187.54	185.14	182.14	178.14	176.14
$p^{atms.}_{Cardoso}$	43.85	42.03	38.88	35.40	31.00	29.40
$p^{atms.}_{cal.}$	43.226	41.242	38.312	34.847	30.577	28.586
Δp	.624	.788	.568	.553	.422	.814
ΔT	.49	.63	.48	.49	.42	.84

Mean $\Delta T = 0.56$

Correcting	T crit. of Cardoso gives	−82.29
	T crit. M. I. T.	−82.11
	Olszewski 1885	−81.8
	p crit. Cardoso	45.6 atms. ±0.1
	p crit. M. I. T.	45.8 atms.

* Cardoso, in verifying the readings of his pentane thermometer, used the freezing point of toluene, accepting a value for the freezing point, due to Timmermans, in 1912, of −94.5. In this laboratory, there has been found for pure toluene −95.70 referred to the H_2 constant volume scale. Recently Timmermans, Van der Horst and Onnes (Chem. Ab. June 10, p. 1694, 1922) give −95.1.

table that the critical pressure given by Cardoso is in good agreement with the pressure observed in this investigation. The temperature of the critical condition would, of course, be independent of any thermometer and a correction of 0.56 applied to the critical temperature, as observed with the pentane thermometer, would give −82.29, which is not in bad agreement with −82.11 obtained in these measurements, since the temperature of the critical phenomenon is difficult to locate exactly and, moreover Cardoso has shown that it is best to stir the liquid in observing

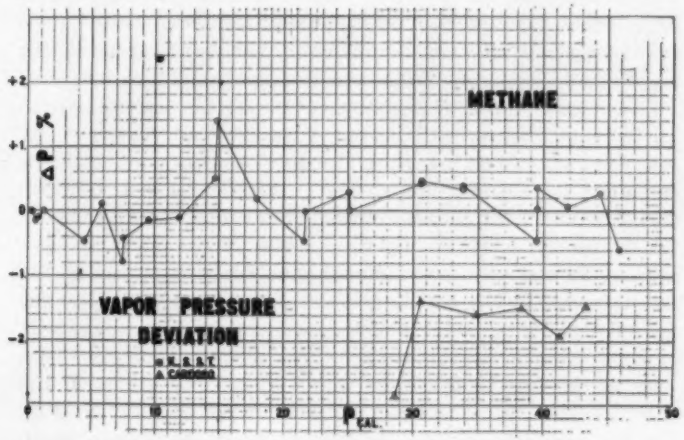


Fig. 4

the critical temperature, whereas in this work no stirring was employed. In the section wherein the densities of liquid methane are presented it will be shown that a correction of about 0.6° in Cardoso's temperature brings his densities into good agreement with the new values.

In Fig. 4 the deviations of the individual pressure measurements of Tables 1 and 2 from the pressures calculated by means of Equation (3) are presented. The results obtained by Cardoso have been also inserted. It is evident that Equation (3) represents the new measurements as satisfactorily as can be expected.

5. **The Specific Volumes of the Liquid and Vapor Phases.** The apparatus, Fig. 2, used to measure the liquid specific volumes has already been described in connection with the vapor pressures. The method is of general applicability for the measurement of the liquid specific volumes for all substances whose critical temperature lies below the freezing point of mercury. The procedure, however, of confining the liquid in the volumenometer E by means of the gas phase requires that the mass of fluid in the gas phase, including that portion in the reservoir F, be determinable from a knowledge of its pressure, volume and temperature. This requirement has been met, in the present instance, from a knowledge of the methane equation of state, but empirical use of the experimental isotherms of gaseous methane could also be made.

The volume of the volumenometer between the engraved marks on the capillaries was 1.5798 cc., while the used volume of the reservoir was about 56 cc. The total quantity of methane employed amounted to about 0.66 g. to 0.78 g., most of which would reside in the volumenometer at the lowest temperatures, but in the bell F at the highest. Owing to the relatively large fraction of the total mass of methane being contained in the reservoir and in the capillary leads of the volumenometer, the accuracy of the specific volume measurements becomes rapidly impaired near the critical temperature. Measurements, however, were carried out to 190.38 or within about 0.65 degree of the critical temperature. The latter temperature was observed directly, but the reliability of the observation would have been much enhanced by stirring the fluid, as has been pointed out in particular by Cardoso.

The actual density measurements for the two series of measurements are presented in Table V. For the greater part two observations at the same temperature setting were made at different times, which give a means of judging of the reproducibility of the method. It will be observed that the concordance is satisfactory on the whole, although in some instances (181.20°, Series A) a large difference (one part in 230) occurs. On the average, however, one part in fifteen hundred or better is attainable in individual measurements. The entire range of the liquid phase has been practically covered and the " smoothed values " are those obtained

TABLE V

Methane Liquid Densities

Series A			*Series B*		
Temperature Deg. Abs.	*Density Liquid gm./c.c. Obs.*	*Density Liquid gm./c.c. Smoothed*	*Temperature Deg. Abs.*	*Density Liquid gm./c.c. Obs.*	*Density Liquid gm./c.c. Smoothed*
186.143	.2505	.2504	128.562	.3980	.3989
186.143	.2504	.2504	128.562	.3979	.3989
181.203	.2768	.2762	123.911	.4051	.4059
181.203	.2756	.2762	123.911	.4049	.4059
178.189	.2882	.2881	119.249	.4129	.4128
178.189	.2879	.2881	119.249	.4127	.4128
172.437	.3067	.3067	114.631	.4196	.4196
172.437	.3067	.3067	114.631	.4195	.4196
168.351	.3186	.3182	110.023	.4266	.4263
168.351	.3185	.3182	110.023	.4262	.4263
163.295	.3312	.3312	106.003	.4313	.4321
163.295	.3313	.3312	105.451	.4329	.4329
158.339	.3429	.3429	100.903	.4394	.4394
158.339	.3426	.3429	153.193	.3542	.3544
153.385	.3531	.3540	158.171	.3439	.3433
153.385	.3531	.3540	181.100	.2768	.2766
148.439	.3631	.3644	186.054	.2510	.2509
143.495	.3752	.3741	187.974	.2366	.2375
143.495	.3750	.3741	188.937	.2279	
138.558	.3828	.3829	189.902	.2170	
138.558	.3832	.3829	190.381	.2093	
133.628	.3907	.3910			
133.628	.3909	.3910			
128.704	.3985	.3987			
128.704	.4000	.3987			

by plotting the densities rather than the specific volumes. Two densities at the extreme temperature ends of the liquid phase were chosen, and a linear equation determined from which deviations of each observed datum could be computed. By plotting these deviations with the corresponding temperatures a smooth curve could be drawn, from which the values tabulated as smoothed were read. The device is evidently equivalent to the construction of a very large plot of the observed data.

There have been found in the literature only the data of Cardoso already briefly referred to in the section dealing with the vapor pressure. It was pointed out in the latter section that the temperatures recorded by Cardoso appeared by comparison of the

TABLE VI

The Cardoso Saturation Specific Volumes

T	V_1 *Cardoso*	V_2 *Cardoso*	V_1 *M.I.T. from Mean Dens. Equa.*	V_2 *M.I.T.*	*Cardoso* V_1 *Corr.*	*Cardoso* V_2 *Corr.*
166.1	32.05	3.085	32.85	3.076	32.92	3.071
173.1	23.20	3.307	23.75	3.280	23.80	3.288
178.1	18.80	3.500	19.02	3.465	19.29	3.476
179.1	17.18	3.559	18.15	3.510	17.65	3.532
183.1	14.73	3.791	15.05	3.732	15.15	3.752
187.1	10.96	4.198	12.25	4.110	11.33	4.147
188.1	10.08	4.371				
189.1	9.15	4.628				

pressures to differ by 0.56° from the temperature scale used in this investigation. A shift in the Cardoso temperature scale of equal amount in this instance also brings the latter's observations into agreement with those here presented, thus confirming the opinion already stated that it is the temperature scales which are in disagreement rather than the pressure or volume measurements. In Table VI the second column gives the vapor volumes as given for the temperatures specified by Cardoso. The third column gives the Cardoso liquid volumes. Columns four and five contain the vapor and liquid volumes obtained in the present investigation at the same temperatures, and the sixth and seventh columns, the volumes of Cardoso corrected for the temperature difference 0.56. It is seen that substantial agreement is obtained, as was the case with the vapor pressures.

The specific volumes of the saturated vapor have always been exceedingly difficult to measure. The difficulty of obtaining true equilibrium, freedom from foreign gases, the complete drainage of the walls of the container, the relatively large fraction of the total mass necessarily present in the liquid phase, and surface adsorption are some of the difficulties encountered. Experimental experience has led almost to the conviction that the vapor specific volume cannot be accurately measured. In the case of ammonia it was found that the equation of state gave saturated vapor specific volumes which accorded with the actual observation within the unavoidable errors of experiment and the same statement is true as regards carbon dioxide.[9] At the low temperatures

9 Keyes and Kenney, Jour. of Soc. Am. Ref. Engr., **3**, 1, 1917.

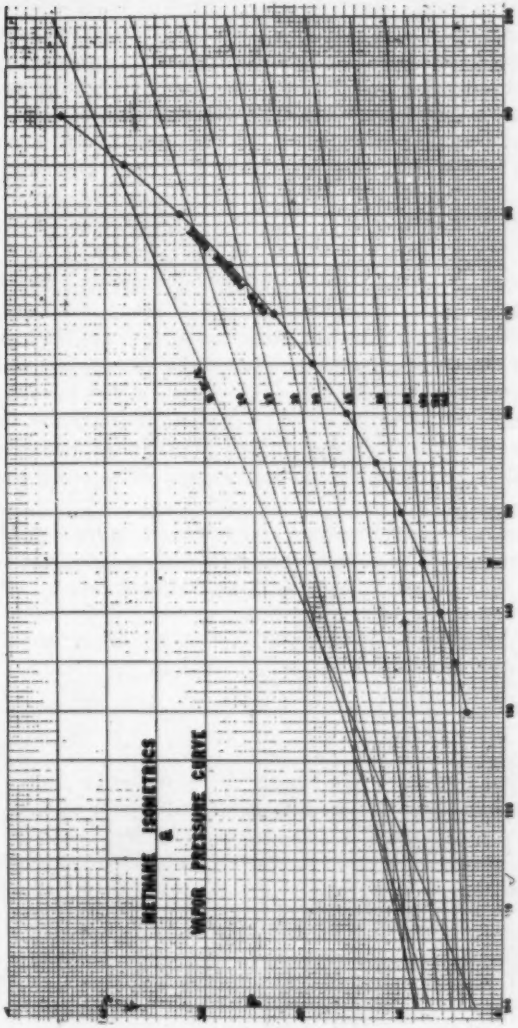


Fig. 5

encountered in the liquid range of methane some apprehension was felt concerning the reliability of using the methane equation of state to calculate the saturation specific volumes, but the enhanced difficulties of carrying out measurements at such low temperatures lead to the decision to calculate the volumes. In the case of nitrogen whose equation of state we possess, values are obtained which, when employed in the Clapeyron equation, give a value for the latent heat of vaporization agreeing well with the experimental number. It is, of course, evident that for the very large specific volumes (1,000 c.c./g.) the equation of state would be accurate. The doubt which may arise pertains to volumes from 200 c.c./g. to 30 c.c./g.

The plot of a number of the isometrics of methane is represented in Fig. 5, upon which has been placed the vapor pressures. The saturation specific volumes are the points of intersection of the isometrics with the pressure-temperature curve and this is, perhaps, the most convenient means of obtaining the vapor specific volumes. The final specific volumes for both phases are represented in the plot Fig. 6.

Table VII contains the saturation specific volumes and densities of methane vapor and liquid from 95° to the critical temperature for each five degrees. Volumes smaller than 35 c.c./g. were not

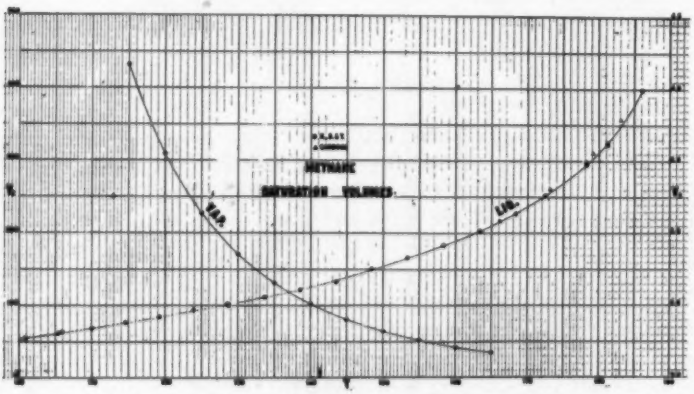


Fig. 6

computed, since association or polymerization may be supposed to exist in the smaller volumes and the equation of state applies only for the case where the completely unassociated methane molecules are present. The mean diameter equation can be used to obtain volumes smaller than 35 c.c./g.

TABLE VII
M. I. T. Methane Data

Temp. Deg. Abs.	*Specific Volume Liquid c.c./gm.*	*Specific Volume sat'd vapor Keyes' eq. c.c./gm.*	*Density Liquid gm./c.c.*	*Density sat'd vapor Keyes' Eq. gm./c.c.*	*Density sat'd vapor from d_m and Liquid Density gm./c.c.*
95		2436.7		.0004104	
100	2.2691	1470.4	.4417	.0006801	
105	2.3069	936.9	.4335	.001067	
110	2.3458	624.7	.4263	.001601	
111.52	2.3580	556.9	.4241	.001796	
115	2.3865	432.7	.4190	.002311	
120	2.4291	309.4	.4117	.003232	
125	2.4735	227.4	.4043	.004398	
130	2.5208	171.0	.3967	.005850	
135	2.5719	131.0	.3888	.007632	
140	2.6288	102.1	.3804	.009794	
145	2.6937	80.63	.3712	.01240	
150	2.7683	64.43	.3612	.01552	
155	2.8533	51.96	.3505	.01925	
160	2.9491	42.22	.3391	.02369	
165	3.0496	34.49	.3279	.02899	
170	3.1881		.3137		.03667
175	3.3463		.2988		.04592
180	3.5565		.2812		.05598
185	3.8871		.2573		.07335
190					
191.03 Crit.	6.2		.1613		.1613

The data of Cardoso relative to the saturation volumes were taken close to the critical temperature. However, in the range where the specific volumes were computed by means of the equation of state the following mean density equation was obtained:

$$Dm = 0.16134 + 0.00065723\ (Tc - T)$$

Cardoso gives the mean density equation based on his results,

$$Dm = 0.1623 + 0.0006064\ (Tc - T).$$

The agreement is very good and lends confidence to the computed

values. Fig. 7 gives the densities obtained in the present investigation together with the uncorrected Cardoso values. The critical density, making the temperature correction 0.56, makes the critical density of Cardoso 0.1618, as compared with 0.1613 obtained in the present investigation.

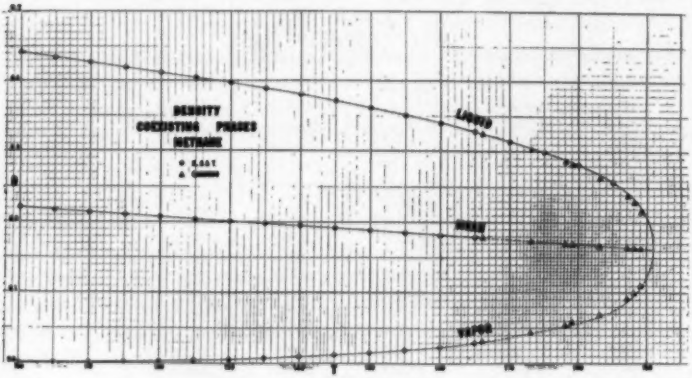


Fig. 7

6. **The Latent Heats of Evaporation.** A preliminary study has been made in the development of calorimetric methods that will permit the measurement of heats of evaporation and the specific heats of liquids at very low temperatures. At present, however, no experimental values are available for methane, but by means of the vapor pressure equation and the specific volumes of the coexisting phases, latent heats may be calculated by means of the Clapeyron equation.

The equation of the vapor pressure, (3), upon differentiation gives for $\frac{dp}{dt}$,

$$\frac{dp}{dT} = p\left[\frac{1371.298}{T^2} - 0.093065 + 7.76685\times10^{-4}T - 1.73878\times10^{-6}T^2\right]. \tag{4}$$

In Table VIII will be found in the first column the absolute temperature and in the succeeding columns the value of $\frac{dp}{dT}$,

TABLE VIII

Latent Heat of Evaporation

T	$\frac{dp}{dT}$ atms.	$V_1 \frac{c.c.}{g.}$	$V_2 \frac{c.c.}{g.}$	$\lambda \frac{cal.}{g.}$	calc.
100	0.03593	1470.4	2.2691	127.75	127.59
105	0.05290	936.9	2.3068	125.71	125.71
110	0.07461	624.7	2.3458	123.69	123.76
111.52	0.08214	556.8	2.3580	122.99	Normal Boiling Pt.
115	0.10152	432.7	2.3868	121.65	121.74
120	0.13403	309.4	2.4291	119.58	119.64
125	0.17249	227.4	2.4735	117.44	117.44
130	0.21723	171.0	2.5208	115.19	115.14
135	0.26856	131.0	2.5719	112.79	112.71
140	0.32677	102.7	2.6288	110.20	110.14
145	0.39214	80.6	2.6937	107.32	107.39
150	0.46493	64.4	2.7683	104.14	104.44
155	0.54535	51.96	2.8533	100.52	101.23
160	0.63363	42.22	2.9491	96.42	97.70
165	0.72975	34.49	3.0496	91.68	93.74

V_1, V_2 and the latent heat. On the basis of these latent heat values the following equation was composed relating the quantity to the temperature:

$$\log_{10}\lambda = 1.65214 + 2.0076 \times 10^{-4}(Tc - T) + 0.22225 \log_{10}(Tc - T). \quad (5)$$

There are no published data for the latent heat of evaporation of methane with the exception of an approximate value recently obtained due to Satterly and Patterson[10] who give 138 cal./g. $\pm 5\%$. This value refers to the temperature of the normal boiling point 111.52° at which temperature 123 cal./g. is obtained in the present investigation. The experimental value is about ten per cent greater. The value of the mean specific heat of copper is involved in the measurement and an error in the true boiling point of methane enters in computing the latent heat from the experimental data. The methane evolved by the copper block dropped into the liquid was measured by collecting over water. In a later paper experimental values obtained in this laboratory will be presented.

If the liquid phase consisted of completely polymerized double molecules or, in fact, was composed of molecules whose molecular

[10] Satterly and Patterson, Roy. Soc. Can. Trans. **13**, 123, 1919.

species was constant with respect to temperature changes the internal heat of evaporation would be simply related to the specific volumes of the coexisting phases. Consider the thermodynamic equation:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p. \tag{6}$$

Integration of this equation at constant temperature yields,

$$U_2 - U_1 = \int_{v_1}^{v_2}\left(T\left(\frac{\partial p}{\partial T}\right)_v - p\right)dv \tag{7}$$

and for an invariable species composing the liquid phase of specific volume, v_2, passing to a specific volume v_1 of the vapor phase the energy is represented by the work against the attractive forces of the molecules. Evaluating $\left(\frac{\partial p}{\partial T}\right)_v$ by means of the equation of state will give, then, a definite value for the right-hand member of Equation (7).

$$\int_{v_1}^{v_2}\left(T\frac{\partial p}{\partial T} - p\right)dv = \int_{v_1}^{v_2}\left(\frac{RT}{v-\delta} - p\right)dv = \int_{v_1}^{v_2}\frac{A}{(v-l)^2}dv,$$

or

$$\Delta U = U_1 - U_2 = A\left(\frac{1}{v_2 - l} - \frac{1}{v_1 - l}\right). \tag{8}$$

Now ΔU and the specific volumes of the coexisting phases may be plotted with $\frac{1}{\Delta U}$ and v_2 as coördinates giving a line which may be used as an approximation plot to roughly evaluate l and A and the data replotted, using as coördinates $\frac{1}{\Delta U + \frac{A}{v_1}}$ and v_2. The fact that a straight line is obtained may mean that the molecular state of the liquid is the same as that of the vapor in contact therewith, or it may mean that the molecular state of the liquid, for example, was that of substantially complete polymerization to double molecules or those of higher order; the vapor in

contact consisting of substantially all single molecules. The value of A in the latter case would be a certain mean value, then, between the value of A for double molecules and single molecules. If the liquid, however, was composed of molecules of the same type as the vapor, the value of A should be numerically equal to

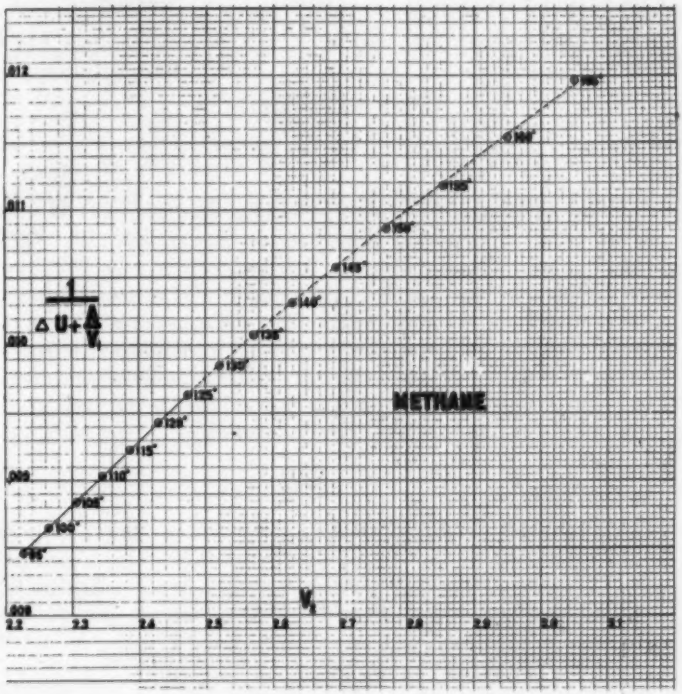


Fig. 8

A obtained for the equation of state of methane. Moreover, if the data do not lie on a straight line in terms of the coördinates given, evidence is afforded that the relative molecular state in the coexisting phases is changing at higher temperatures. As a matter of fact the data of methane in the lower temperature range do lie on a straight line, but deviate as higher temperatures

are approached. Also the numerical value of A is not that found for the equation of state of methane composed of single molecules. Fig. 8 exhibits the methane data.

The further elaboration of the connection between the internal heat of evaporation and the equation of state has been waiting for some years for the completion of several investigations in progress in this laboratory. Very shortly, for example, there will appear the results in connection with liquid ether at low temperatures, which illustrate the linear relation between $\frac{1}{\Delta U+\frac{A}{v_1}}$ and v_2, and further papers, it is hoped, will follow promptly.

7. **The Specific Heats of the Coexisting Phases.** The experimental data for the vapor phase have been published by Regnault,[11] Lussana[12] and Heuse.[13] The latter data supersede the older work and measurements were made at the temperatures 15.0, 5.0, −30.0, −55.0, −81.0. The one atmosphere constant pressure values were computed to constant volume specific heats by means of the equation of state and from a plot values chosen at the absolute temperatures 150, 200, 250, 300 for the purpose of correlation as a function of the temperature. The equation obtained is,

$$C_v=0.3050+1.12\times10^{-3}T-6.45\times10^{-6}T^2+13.04\times10^{-9}T^3. \quad (9)$$

To obtain the constant pressure specific heat use may be made of the equation

$$C_p=C_v+T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p \quad (10)$$

which becomes using the equation of state for methane:

$$C_p=C_v+\frac{R/m}{1-\frac{a\delta}{v^2}-\frac{2A}{RT}\frac{(v-\delta)^2}{(v+l)^3}}. \quad (11)$$

This equation is not valid in the critical region but will give accurate values along the saturation line to at least 35 c.c. per

[11] Regnault. Mem. de l'Acad. **26**, 1, 1862.
[12] Lussana. Nouv. Cim. **36**, 5, 70, 130, 1894.
[13] Heuse. Ann. d. Phy. **59**, 94, 1919.

gram. For low pressures it suffices to replace (11) by the approximate equation:

$$C_p = C_{p_0} + \frac{2A}{R} \cdot \frac{1}{T^2} p \tag{12}$$

where C_{p_0} is the specific heat at very low pressures, being equal to $C_v + R/m$; m representing the molecular weight in grams and R the gas constant per mol in calories. The numerical equation corresponding to (12) is,

$$C_p = 0.4288 + 1.12 \times 10^{-3} T$$
$$- 6.45 \times 10^{-6} T^2 + 13.04 \times 10^{-9} T^3 + \frac{93}{T^2} p^{\text{atm.}} \tag{13}$$

In Table IX will be found the comparison of the vapor specific heats computed by Equation (9) and the experimental values due to Heuse.

TABLE IX

The Gas Phase Specific Heat

	15.0	5.0	−30.0	−55.0	−81.0
C_p Heuse	0.4051	0.4000	0.3826	0.3782	0.3777
C_p Calculated	0.4041	0.3982	0.3834	0.3778	0.3746

Regnault gives 0.593 cal. as the value of C_p between 18 and 208 at one atmosphere. Equation (13), however, leads to 0.675 cal. Lussana gives 0.591 cal. between 11 and 95 at one atmosphere, whereas the equation gives 0.564 cal. Lussana gives the specific heat between 11 and 95 as a function of the pressure, as follows:

$$C_p = 0.5915 + 0.03463(p - 1)$$

whereas Equation (13) leads to

$$C_p = 0.5643 + 0.00089(p - 1).$$

The pressure coefficient of Lussana is nearly forty times as large as that given through the equation of state. In the case of air Lussana's pressure coefficient is also much greater than that given by the equation of state for air.[14] Holborn and Jacobs,[15]

[14] Keyes, Jour. Amer. Chem. Soc. **43**, 1452, 1921.
[15] Holborn and Jacobs, Z. Ver. deut. Ing. **58**, 1429, 1914.

however, recently measured the specific heat of air to 200 atms. and their mean pressure coefficient agrees almost exactly with that given through the equation of state. Carbon dioxide and ammonia furnished further examples and there can be little doubt but that Lussana's pressure coefficients are all too large.

Facilities for measuring the specific heat of the liquid phase of substances have been under development for some years and shortly values will be available. In the meantime use may be made of the available data to calculate the liquid phase specific heat.

Consider the thermodynamic equation

$$C_{s_1} - C_{s_2} = T\frac{d\frac{\lambda}{T}}{dT} \tag{14}$$

where C_{s_1} and C_{s_2} denote the specific heat of the saturated gas and liquid phases respectively, while λ as before represents the latent heat of evaporation. The equation for C_{s_1} is,

$$C_{s_1} = C_{p_1} - T\left(\frac{\partial v}{\partial T}\right)_p \frac{dp}{dT}$$

and $C_{p_1} = C_{v_1} + T\left(\frac{\partial p}{\partial T}\right) \cdot \left(\frac{\partial v}{\partial T}\right)$. By means of the equation of state the differential coefficients can be evaluated, while C_v is given by the equation (9). The equation for $T\frac{d\frac{\lambda}{T}}{dT}$ can be formed from Equation (5) leading to

$$T\frac{d\frac{\lambda}{T}}{dT} = -\lambda\left[0.0004623 + \frac{0.22225}{T_c - T} + \frac{1}{T}\right].$$

At 110° C_{s_1} is $-0.689\ \frac{\text{cal.}}{\text{g.}}$ and $T\frac{d\frac{\lambda}{T}}{dT}$ equal to -1.522, giving C_{s_2}, the specific heat of the liquid, $0.833\frac{\text{cal.}}{\text{g.}}$. At 150° C_{s_1} is $-0.489\ \frac{\text{cal.}}{\text{g.}}$ and $T\frac{d\frac{\lambda}{T}}{dT}$ equal to -1.307 giving $0.818\ \frac{\text{cal.}}{\text{g.}}$ for the liquid specific

heat. The latter number would be expected to be larger than the former, but the specific heat value at 110° involves a long extrapolation by means of the gas phase constant volume specific heat Equation, (9). All that may be stated at present is that in the region of the boiling point the specific heat of the liquid is about $0.82\frac{\text{cal.}}{\text{g.}}$

SUMMARY

1. The vapor pressure of methane has been measured over substantially the entire liquid phase region and correlated as a function of the temperature as follows:

$$\log_{10} p^{\text{atm.}} = -\frac{595.546}{T} + 8.09938 - 4.04175 \times 10^{-3} T + 1.68655 \times 10^{-4} T^2 - 2.51715 \times 10^{-7} T^3.$$

2. The liquid phase specific volumes have been measured from about 100° abs. to nearly the critical temperature, 191.03 abs. The saturation specific volumes of the vapor phase were computed by means of the equation of state of methane, using the values of the pressure computed for definite temperatures from the vapor pressure equation.

3. The critical temperature is found to be 191.03° abs. on the scale of the quartz constant volume hydrogen thermometer. The critical pressure amounts to 45.8 atms., while the critical volume computed from the mean diameter equation is 6.2 c.c./g.

4. The heat of evaporation was computed by the Clapeyron equation, using the derivative $\frac{dp}{dT}$ obtained by differentiation of the vapor pressure equation and the specific volumes of the coexisting phases. The following equation reproduces the values from 100° abs. to 150° abs. where λ represents the heat of evaporation:

$$\log_{10} \lambda = 1.65214 + 2.0076 \times 10^{-4} (T_c - T) + 0.22225 \log_{10} (T_c - T).$$

5. The specific heat of the gas phases may be represented by the following equation based on the experimental values of Heuse:

$$C_v = 0.3050 + 1.12 \times 10^{-3} T - 6.45 \times 10^{-6} T^2 + 13.04 \times 10^{-9} T^3.$$

6. The specific heat of the saturated liquid was computed by means of the thermodynamic equation

$$C_{s_2} = C_{s_1} - T \frac{d \overset{\Delta}{T}}{dT}$$

and found to be $0.82 \frac{\text{cal.}}{\text{g.}}$ in the neighborhood of the normal boiling point.

(Contribution from the Rogers Laboratory of Physics, Massachusetts Institute of Technology.)

THE ESTABLISHING OF THE ABSOLUTE TEMPERATURE SCALE BELOW THE MELTING POINT OF ICE

By FREDERICK G. KEYES, BAILEY TOWNSHEND AND LOUIS H. YOUNG

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Part II

Freezing Points of Certain Organic Liquids and of Mercury and Ammonia.

The Method.

The Results.

Summary.

I. Introduction

The field of experimental inquiry at low temperatures relative to the properties of matter is one which has benefited largely from the researches conducted at Professor Onnes' laboratory in Leiden. Here there have been developed ingenious methods for attacking the many varied problems among which the most fundamental is undoubtedly the devising of convenient and accurate temperature-measuring instruments, and the relating of their indications to the absolute temperature scale. Systematic investigations of notable importance in the measurement of low temperatures have also been carried out at the Reichsanstalt. The status of the general problem has, however, not reached that stage where the calibration of temperature indicators of the secondary class, such as the electrical resistance, pentane, or thermoelement thermometers, can be safely relied upon without the use of the gas thermometer. The fixed points, for example, worthy of most confidence are the normal boiling points of oxygen and carbon dioxide; the former of which lies at about $-183°$ and the latter at about $-78.5°$. Evidently more fixed points are needed, and, moreover, the investigations of Henning have shown that the platinum resistance thermometer departs in its indications widely from the Callendar formula which is satisfactory above the ice point. Cardoso in the case of the pentane thermometer has also pointed out special difficulties attending the use of this thermometer, so that confidence in the low temperature investigations being carried out in this Institute could only be realized by an independent study of the low-temperature scale.

The many careful researches on gas thermometry and general methods of temperature measurement have dealt in the main, of course, with ordinary and high temperatures, while the region below the ice point has not as yet received as much development as is necessary. Apart, moreover, from the immediate need of thermometric standardization below 0°C. collateral problems have deterred progress in this direction. Chief of these is the relative difficulty of producing low temperatures and the extreme difficulty of maintaining these temperatures constant over considerable periods of time. In gas thermometry there is

also the uncertainty with regard to the expansion of the container of the thermometric substance, and the effect of aggravated adsorption of the gas on the walls of the thermometer bulb. Indeed, it will be shown that this latter effect may be very appreciable and leads to serious error in the case of gases readily adsorbed. For some time this laboratory has had developed an improved type of cryostat wherein constancy of temperature of 0.01°C. is easily attainable, and certain other instrumental refinements, making it worth while to study the subject independently, from a slightly different standpoint, and with a view to increasing the accuracy of low temperature measurements.

The investigation set forth in the following pages has had for its primary objects: first, a study of the gas thermometer of constant volume between 0°C. and the boiling point of oxygen (−183°) and, second, the determination of certain fixed points within this range serving the same purpose as those now available for calibration of secondary instruments at temperatures above the ice point. Incident hereto was, of course, a comparison of the platinum resistance thermometer and copper-constantan thermocouple used in other low temperature investigations with the hydrogen constant volume thermometric scale.

II. **Calculation of Temperature from Observed Measurements with the Constant Volume Gas Thermometer.** Centigrade temperature is defined by the equation:

$$t = \frac{p - p_0}{\epsilon^t_0 p_0} \tag{1}$$

where p and p_0 are the pressures exerted by the gas at $t°$ and 0° respectively, and ϵ^t_0 is the mean coefficient of pressure increase at constant volume between 0° and $t°$. The two fixed points defined by the freezing point and normal boiling point of water are, of course, the usual temperature interval used.

Since the volume of the container is not absolutely constant,

owing to temperature dilation and pressure dilation changes, it is necessary to modify (1) to

$$t = \frac{p\frac{v}{v_0} - p_0}{\frac{t}{\xi_0} p_0} \qquad (2)$$

where v and v_0 are the true volumes at $t°$ and 0°.

The system containing the gas comprises the bulb of the thermometer and a certain length of capillary connecting the bulb to the manometer. Let the volume of this latter part be designated as "dead space" and the following symbols adopted:

V_0 = volume of bulb at 0°.
V = volume of bulb at $t°$.
v_s = volume of dead space at room temperature.[1]
β = coefficient of cubical expansion of bulb material.
δ = coefficient of expansion of the bulb with internal pressure (c.c. per mm.)

Then (2) becomes

$$t = \frac{1}{\frac{t}{\xi_0} p_0}\left[p\frac{V_0+v_s}{V_0+v_s} - p_0\right]$$

or

$$t = \frac{1}{\frac{t}{\xi_0} p_0}\left[p\left\{1+\frac{\beta t V_0+\delta(p-p_0)}{V_0+v_s}\right\} - p_0\right] \quad . \quad . \quad . \quad (3)$$

Dead Space Correction

In the above formula the pressures are those which the gas would exert if the entire volume were at $t°$ and 0° respectively. In practice, the bulb and a certain portion of the capillary are at the temperature of the bath, while the remainder of the dead space may be divided into parts at $t°_1$, $t°_2$, etc. The manner of computing p from the corrected observed pressure, p', is as follows: Let

[1] The volume of the dead space is relatively small and since the temperature of the greater part of it is always within a few degrees of the same value it is not necessary to consider its volume change due to temperature and pressure.

V = volume of the bulb at the temperature of the bath, t.
v_1, v_2, etc. = volumes of dead space at corresponding temperature, t_1, t_2, etc.
ϵ = approximate coefficient of expansion of a gas, 0.00366.

Then, making use of the fact that the total mass of gas in the apparatus is constant:

$$p\frac{(V+v_1+v_2+\ \ldots)}{1+\epsilon t}=\frac{p'V}{1+\epsilon t}+\frac{p'v_1}{1+\epsilon t_1}+\frac{p'v_2}{1+\epsilon t_2}+\ \ldots$$

from which it follows that:

$$p-p'=p'\left\{\frac{v_1(1+\epsilon t_2)(t-t_1)\epsilon+v_2(1+\epsilon t_2)(t_1-t_2)\epsilon}{(V+v_1+v_2)(1+\epsilon t_1)(1+\epsilon t_2)}\right\}\ \ldots \qquad (4)$$

where the dead space is considered in this example as consisting of two portions, v_1 and v_2.

Correction of the Observed Pressure

The pressures are here expressed in millimeters of mercury. To obtain p' the actually observed height must be corrected to millimeters of Hg at 0°, sea level, and 45° latitude and also for difference in level of the bulb and contact point of the manometer.[2] The former involves a knowledge of calibration errors and coefficient of expansion of the cathetometer scale. Let

γ = coefficient of linear expansion of cathetometer scale.
σ = scale error per millimeter as compared with standard scale at 20°.
p^{IV} = actually observed pressure.
p^{III} = pressure corrected for cathetometer scale errors.
t_r = room temperature.

then

$$p^{III}=p^{IV}\{1+\sigma+\gamma(t_r-20)\} \qquad (5a)$$

[2] A correction for capillary depression may be eliminated by using manometer tubes of sufficiently large and uniform diameter.

Further let

t_m = temperature of mercury column of manometer.
a = mean coefficient of expansion of mercury 0° to $t_m°$.
g = acceleration of gravity at place of observation.
G = standard acceleration of gravity.
p^{II} = pressure corrected for scale errors and reduced to standard conditions.

Then

$$p^{II} = p^{III}\left(\frac{g}{G}\right)\left(1 - at_m\right) \tag{5b}$$

The level correction is significant where the difference in level is several hundred millimeters. Let

l = height of bulb above contact point of manometer.
ρ_g = density of the gas at temperature of column 1.
ρ_m = density of mercury at 0°.
p = pressure corrected for scale errors, reduced to standard conditions, and corrected for difference in gas level.

Then

$$p^{I} = p^{II} - \frac{\rho_g l}{\rho_m} \tag{5c}$$

Combining into one formula the various corrections applicable to the observed height, $p,^{IV}$ and excepting the dead space correction, there results:

$$p^{I} = p^{IV}\left\{1 + \sigma + \gamma(t_r - 20)\right\}\left(\frac{g}{G}\right)\left(1 - at_m\right) - \frac{\rho_g l}{\rho_m} \tag{6}$$

Formulæ (3), (4) and (6) thus serve to calculate the centigrade temperatures from the actually observed difference in height of the mercury columns of the manometer, it being assumed that the space above the variable column is exhausted.

A quantitative discussion of sources of error will be given in connection with the description of the experimental procedure. It will be, however, instructive at this point to present a sample calculation illustrating the magnitudes of the various corrections.

The following is a measurement of the temperature of liquid oxygen (above its normal boiling point) by means of the hydrogen thermometer.

p^{IV} mm.	t_m	t_r	*Time* (3/30/22)
255.430	23.16	25.0	10.50
255.423	23.17	25.0	.52
233.430	23.18	25.0	.57
255.435	23.20	25.0	.59

For the correction for scale and reduction of mercury column to standard conditions (5a), (5b),

$$p^{II} = 255.430\,[1+20\times10^{-6}+11\times10^{-6}(25-10)][1-0.000255]\,[1-1.809\times10^{-4}(23.18)]$$
$$= 254.313 \text{ mm.}$$

For the correction for difference in level of the bulb and contact point of manometer (5c),

$$p^{I} = 254.313 - \frac{0.00038\times300}{13.5}$$
$$= 254.305 \text{ mm.}$$

Correction for dead space:

$$p - p^{I} = 254.3\left[\frac{.0133(1+23.2\epsilon)(-103\epsilon)+.764(1-79.9\epsilon)(-206\epsilon)}{92.7(1+23.2\epsilon)(1-79.9\epsilon)}\right]$$
$$= -1.49 \text{ mm.}$$

Whereupon

$$p = 252.82 \text{ mm.}$$

Calculation of the temperature: $p_0 = 763.17$ mm.

From (3) $\overset{100}{\underset{0}{\epsilon_p}} = 0.0036623$

$$t = \frac{1}{p_0 \overset{t}{\underset{0}{\epsilon_p}}}[252.82(1-0.000013)-763.17] = -182.60°\text{C}$$

III. The Relation Between the Constant Volume Gas Scale and the Kelvin Thermodynamic Scale

The international practical scale of temperature is that of the hydrogen constant volume thermometer with initial pressure (0°C.) of one thousand millimeters of mercury.[3] At the time of this definition, hydrogen was the most nearly "perfect" gas known and the deviations of its scale from the absolute thermodynamic scale were supposedly no greater than the experimental error of gas thermometry. The scientific definition of temperature is contained in the second law of thermodynamics and it becomes a matter of fundamental importance to interpret the temperature indications of the constant volume gas thermometer with the rational thermodynamic scale or Kelvin[4] scale.

Consider the thermodynamic relation expressing the dependence of the internal energy, U, of a gas upon its volume at constant temperature:

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

$$= T^2\left\{\frac{\partial (p/T)}{\partial T}\right\}_v \qquad (7)$$

If $(\delta U/\delta v)_T = 0$ as in the case of the perfect gas, we obtain from (7):

$$\frac{p}{T} - \frac{p_0}{T_0} = 0 \quad \text{at constant volume.}$$

$$T_0(p - p_0) - p_0 t = 0$$

or

$$t = \frac{p - p_0}{\epsilon p_0} \qquad (8)$$

where $\epsilon = 1/T_0$ by definition. (8) gives our fundamental definition of centigrade temperature in terms of the constant volume "perfect gas" thermometer.

For an actual gas $(\delta U/\delta_v)_T \neq 0$ and the gas scale temperature is therefore defined by (1), *viz.*:

$$t = \frac{p - p_0}{\underset{0}{\overset{t}{\int}} \epsilon_v p_0}$$

[3] Comité international des Poids et Mesures, Oct. 15, 1887.
[4] Lord Kelvin, Math. and Phys. Papers, Vol. 1, p. 100, 1848.

Designate the quantity $(\delta U/\delta v)_T$ by λ, where λ may be a function of the absolute temperature, designated by T. Then in general we have for the constant volume thermometer:

$$\frac{p}{T}-\frac{p_0}{T_0}=\int_{T_0}^{T}\frac{\lambda}{T^2}dT \tag{9}$$

Putting, for brevity, $\int_{T_0}^{T}\frac{\lambda}{T^2}dT=I=\frac{T_0(p-p_0)-p_0t}{T\ T_0}$

whence, since $\frac{p-p_0}{p_0t}=\overset{t}{\underset{0}{\epsilon}}_p$, $\quad \overset{t}{\underset{0}{\epsilon}}_p=\epsilon+\frac{T\ I}{p_0t}$ (10)

where ϵ is the expansion coefficient of a perfect gas, or $1/T_0$. Equation (10) would serve to evaluate $\overset{t}{\underset{0}{\epsilon}}_p$ for any gas, provided there were means of determining λ, and hence I. λ has not been successfully measured experimentally.

It is to be noted that the temperature given by (1) is the true centigrade temperature by definition of $\overset{t}{\underset{0}{\epsilon}}_p$. In using this equation it has been customary to put for $\overset{t}{\underset{0}{\epsilon}}_p$ the measured mean pressure coefficient between 0°C. and 100°C., namely, $\overset{100}{\underset{0}{\epsilon}}_p$. In this case there results.

$$t_g=\frac{p-p_0}{\overset{100}{\underset{0}{\epsilon}}_p\ p_0} \tag{11}$$

and

$$t_g-t=t.\ \frac{\overset{t}{\underset{0}{\epsilon}}_p-\overset{100}{\underset{0}{\epsilon}}_p}{\overset{100}{\underset{0}{\epsilon}}_p}$$

Obviously, if the pressure is a linear function of the temperature at constant volume, $t_g-t=0$, and the temperature given by (11) needs no correction.

A. The Equation of State for Gases

Much evidence has recently come to hand, that in a gaseous system composed of invariable species of molecule* the pressure at constant volume actually varies linearly with the temperature. Ramsay and Young[5] reached this conclusion from a study of the ether and carbon dioxide isometrics. The equation of Van der Waals, moreover, is of this form, and the equation of state deduced by Keyes[6,7,8]:

$$p = \frac{RT}{v-\delta} - \frac{A}{(v-l)^2} \tag{12}$$

where $\delta = \beta e^{-a/v}$ for polyatomic gases and $\delta = \beta$ for monatomic gases requires a linear increase of pressure with temperature. The satisfactory agreement of this equation with the experimental data on nitrogen, air argon, hydrogen, helium, carbon dioxide, ammonia, steam, ether, methane, and isopentane make it seem highly probable that it represents the facts well within the experimental error. Once given an equation of state it becomes possible, of course, to calculate such quantities as $\overset{t}{\epsilon}_v$, $\overset{t}{\epsilon}_p$, the Joule-Thomson coefficient μ, $\frac{\partial(pv)}{\partial p}$, and also the absolute ice point temperature, T_o. The agreement of the results of such calculations with experiment furnishes additional and critical evidence of the validity of the form of the equation. With these results the conclusion is reached that the constant volume gas thermometer, operated within the range where the species of molecule is invariable, and where adsorption of the gas upon the walls of the container is not a factor, indicates the absolute thermodynamic temperature without correction.

* *i.e.* dissociation or association must not take place within the contemplated range.

[5] Nature, **44**, pp. 276, 608, 1891 ; also Preston, Theory of Heat (3 ed.), p.460.

[6] Keyes, Proc. Nat. Acad. Sci. **3**, p. 323, 1917.

[7] Phillips, This Jour., **1**, p. 42, 1921.

[8] Keyes, Jour. Am. Soc. Refrig. Engrs., **1**, 9, 1914.
Keyes, Jour. Am. Chem. Soc., **41**, 589, 1919.
Keyes, Jour. Am. Chem. Soc., **42**, 54, 1920.
Keyes, Jour. Am. Soc. Refrig. Engrs. **7**, 371, 1921.
Keyes, Jour. Am. Chem. Soc., **43**, 1452, 1921.
Keyes, This Jour. **1**, 89, 1922.

This conclusion can, however, be subjected to direct experimental test; for if there is a thermodynamic correction it must be proportional to the initial pressure of the gas[9] and may be determined by measuring the same temperature at different initial pressures and extrapolating to zero initial pressure. Thus, if the measured temperatures plotted against the initial pressure give a straight line which is not horizontal, it may be concluded there is a thermodynamic correction. On the other hand, if it is found that a curved line results, the deviations must be laid in part at least to some source other than an intrinsic property of the gas,

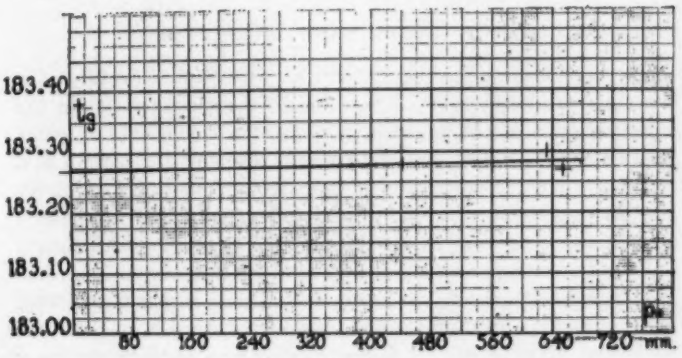

Fig. 1

such as adsorption, or a change in the molecular species of the thermometric gas. Measurements of this sort, using nitrogen as the thermometric gas, for which the correction is supposed to be relatively large, were made. The comparison temperature was that of liquid air, and the readings were referred to the same actual temperature by means of a multiple thermocouple, sensitive to 0.01°C., immersed with the gas thermometer. The mean of several determinations at each initial pressure has been plotted against the initial pressure in Fig. 1. It will be seen that the mean of determinations at approximately 640 mm. agrees with those

[9] F. Henning, Temperaturmessung (F. Vieweg u. Sohn, 1915), p. 67.

at 440 mm. within the experimental error. According to the corrections to the constant volume nitrogen scale calculated by D. Berthelot,[10] however, the measured temperatures at these two initial pressures should have differed by 0.12°. In point of fact they are seen to differ by less than 0.01°.

We shall find that the nitrogen thermometer, however, does differ in its indications from those of the hydrogen thermometer at liquid air temperatures by about as much as 0.6°C. This deviation is explainable by adsorption of the gas on the walls of its container, or polymerization of the nitrogen, as will be shown in discussing the direct comparison of the two thermometers.

B. The Normal Sulfur Boiling Point

The errors that may be introduced by surface effects of the container are impressively illustrated in the discrepancies in the measurements of the pressure and volume coefficients of gases by various observers. For illustration, consider the careful and representative measurements of the boiling point of sulfur by Holborn and Henning[11] and by Eumorfopoulos[12]. The latter used a Callendar constant-pressure nitrogen thermometer with quartz bulbs. The nitrogen was prepared and the instrument loaded in such a way as to insure the purity of the gas. It was found, that after pumping out this loading and evacuating at 500°C, the coefficient of expansion of a new loading was appreciably lower than that of the first. Several repetitions of this process finally reduced the measured coefficient to a constant value. A similar effect was observed in other sets of experiments. In each case, the final value of the coefficient agrees excellently with that calculated by means of the nitrogen equation of state of Keyes (12). These results are shown in the following table. Between successive observations the bulb was heated to 500°C. and thoroughly exhausted. Eumorfopoulos chose the final values of the volume coefficient of each series in the calculation of the temperature of boiling sulfur.

[10]Berthelot, Trav. et Mem. Bur. Int. **13**, 1907.
[11]Holborn and Henning, Ann. d. Phys. **35**, p. 761, 1911.
[12]Eumorfopoulos, Proc. Roy. Soc. **90**, A, p. 189, 1914.

TABLE I

	Initial Pressure mm.	$\frac{100}{\epsilon_\rho}\times 10^7$ *Obs.*	$\frac{100}{\epsilon_\rho}\times 10^7$ *Calc.*	*Obs.-Calc.* $\times 10^7$
First Series	760	36714	36695	19
	763	36702	36696	6
	784	36702	36698	4
Second Series	756	36728	36695	33
	756	36704	36695	9
	757	36701	36995	6
	757	36699	36995	4

The foregoing results clearly indicate the necessity of repeated loading and exhausting at high temperature, and the unreliability of measurements where this precaution has not been taken. The following table gives a comparison of the finally accepted coefficients at the various initial pressures used by Eumorfopoulos with those calculated from the equation of state:

TABLE II

Initial Pressure mm.	*Obs.* $\times 10^7$	*Calc.* $\times 10^7$	*Obs.* $-$ *Calc.* $\times 10^7$
792	36701	36699	2
784	36702	36698	4
757	36699	36695	4
415	36659	36657	2
395	36656	36655	1

By extrapolation of the experimental values to zero pressure, Eumorfopoulos found the coefficient of the perfect gas to be 0.0036613; giving the ice point on the thermodynamic scale as 273.13°C., which is in almost exact agreement with the value calculated by Keyes[13] several years ago from (12), and also obtained by Buckingham[14] from a study of the available Joule-Thomson data.

The normal sulfur boiling point was measured at these different initial pressures and the values extrapolated to zero pressure to obtain the N.B.P. on the thermodynamic scale. Eumorfopoulos found this to be 444.61°C. If we take the various actually observed

[13]Keyes, Jour. Am. Chem. Soc., **42**, 54 (1920).
[14]Buckingham, Bull. Bur. Stand., **3**, 237 (1907).

boiling points and apply to each the thermodynamic correction for the constant pressure nitrogen scale calculated from the equation of state (12) we find the following values:

TABLE III

Initial Pressure mm.	*Temp. Obs.*	*Normal S.B.P. Corr.*
792	444.13	444.53
784	444.14	444.53
757	444.13	444.51
415	444.36	444.57
395	444.39	444.59
		444.55 mean.

Consider the work of Holborn and Henning on this same fixed point. They employed platinum resistance thermometers which had been directly compared with the constant volume gas thermometers of helium, hydrogen and nitrogen. The value obtained from the comparison with helium and hydrogen was 444.51°C. and considered final, since the thermodynamic correction to these scales was assumed less than the experimental error. From the comparison with the nitrogen gas thermometer, however, they found the value 444.43 C. To this value they applied the Berthelot correction, thus bringing it up to 444.59°C. The application of the correction evidently does not diminish the discrepancy between the two values, but merely changes its sign. A study of their results brings out, nevertheless, certain inconsistencies in the measurements of the pressure coefficients of nitrogen. Thus, the mean of the nitrogen coefficients measured in a quartz container at 621 mm. was 0.0036684, whereas two series in Jena glass gave 0.0036704 (at 631 mm.), and 0.0036710 (at 621 mm.). For helium and hydrogen, the measured coefficients were 0.0036618 (at 612 mm.), and 0.0036625 (at 623 mm.) respectively. These coefficients seem too large — for helium and hydrogen only very slightly (1 part in 10,000), for nitrogen decidedly (1 part in 3060) — on comparison with the values computed from (12). If we assume the calculated values correct, the gas thermometer temperatures become 444.55°C. on the helium and hydrogen scales, and 444.57°C

on the nitrogen scale. Using, therefore, the gas expansion coefficients calculated from the equation of state of Keyes, and making no correction to the constant volume thermometer while using the corrections for the constant pressure nitrogen scale as computed by Keyes, there results the following excellent agreement in the sulfur N.B.P.

TABLE IV
Normal Sulfur Boiling Point

Observer	*Gas Thermometer*		*t.*
	Gas	*Constant*	
Holborn and Henning, 1911	He, H_2	Volume	444.55
Holborn and Henning, 1911	N_2	Volume	444.57
Eumorfopoulos, 1914	N_2	Pressure	444.55

C. The Usual Corrections to the Constant Volume Thermometer

The discussion of this subject would be incomplete without a critical review of the methods which have been used by Rose-Innes[15], Berthelot[16], Buckingham[17], and Callendar[18] in computing corrections for constant pressure and constant volume gas thermometers.*

Rose-Innes assumed that the Joule-Thomson data for hydrogen and nitrogen could be represented by

$$\mu C_p^{**} = a_0 + \frac{a_1}{T} + \frac{a_2}{T_2}$$

From this an equation of state

$$pv = RT - p\left[a_0 + \frac{a_1}{2T} + \frac{a_2}{3T^2}\right]$$

[15] Rose-Innes, Phil. Mag. (6), **2**, p. 130, 1901 and Phil. Mag. (6), *15*, p. 301, 1908.
[16] Berthelot, Mem. Trav. Bur. Int., **13**, 1907.
[17] Buckingham, Bull. Bur. Stan., **3**, 237, 1907.
[18] Callendar, Phil. Mag. (6), **5**, p. 48, 1903.

* For a resumé of the various methods see Henning, Temperaturmessung, p. 72.

** μC_p is defined from the thermodynamic equation for the Joule-Thomson effect, namely,

$$\mu C_p = \frac{\partial T}{\partial p} \cdot C_p = T\left(\frac{\partial v}{\partial T}\right)_p - v.$$

is derived subject to the condition that

$$\left\{\frac{\partial(pv)}{\partial p}\right\}_T = -\left[a_0+\frac{a_1}{2T}+\frac{a_2}{3T^2}\right]$$

It follows then that the correction to the constant volume scale is

$$[t_g]_v - t = \frac{a_2}{3v}\,\frac{(t-t_0)(t-t_1)}{tt_0t_1}$$

and the correction to the constant pressure scale is

$$[t_g]_p - t = \frac{(t-t_0)(t-t_1)}{tt_1}\left\{\frac{a_1}{2V_0}+\frac{a_2}{3V_0}\left(\frac{1}{t}+\frac{1}{t_0}+\frac{1}{t_1}\right)\right\}$$

where the subscripts 0 and 1 refer to the freezing and boiling points of water. The constants a_0, a_1, a_2 were evaluated from Joule-Thomson data and the compressibility data of Amagat and of Chappuis.

Berthelot, on the assumption that the isotherms (pv, p) are straight lines within the region of gas thermometer pressure, found the following correction equations:

$$[t_g]_v - t = p_0\left[273(t-100)\left\{\frac{\partial(pv)}{\partial p}\right\}_0 - 3.73t\left\{\frac{\partial(pv)}{\partial p}\right\}_{100} + (273+t)\left\{\frac{\partial(pv)}{\partial p}\right\}_t\right]$$

$$[t_g]_p - t = 2.73p_0\left[(t-100)\left\{\frac{\partial(pv)}{\partial p}\right\}_0 - t\left\{\frac{\partial(pv)}{\partial p}\right\}_{100} + 100\left\{\frac{\partial(pv)}{\partial p}\right\}\right]$$

Values of $\frac{\partial(pv)}{\partial p}$ were taken from various sources, and the range extended by means of the law of corresponding states.

Buckingham extended the range of Joule-Thomson coefficients by means of the law of corresponding states, and then calculated the correction to the constant pressure thermometer from the relation.

$$t-[t_g]_p=[t_g]_p\frac{T_0-T'_0}{T_1}-T'\frac{p_0}{R}\int_{T'_0}^{T'}\frac{\mu' C_p dT'}{T'}$$

The corrections* to the constant volume scale were derived from a combination of the above with isothermal data, according to the relation

$$[t_g]_p-[t_g]_v=[t_g]_v\frac{\epsilon_v^{100}}{\epsilon_0^{100}}\left[\frac{\epsilon_v^{100}-\epsilon_0^{100}}{\epsilon_0^{100}}-p_0\left(\frac{\partial(pv)}{\partial p}\right)\right]$$

To obtain $\left\{\frac{\partial(pv)}{\partial p}\right\}_t$ Buckingham used the equation of Berthelot: on the other hand $\left\{\frac{\partial(pv)}{\partial p}\right\}_T=b-\frac{a}{RT^2}$

Callendar, on the other hand, based his calculations upon an equation of state of the Clausius-Nerthelot form

$$pv=RT+p\left(b-\frac{a}{RT^n}\right)$$

where n was taken as a characteristic constant of the gas, 0.5 for monatomic, 1.5 for diatomic, and 2.3 for polyatomic gases.

The two outstanding features of the four investigations outlined above are: (1) the assumption of a $\left(\frac{\partial(pv)}{\partial p}\right)_T$ function at ordinary pressures in inverse powers of T, and (2) the assumption of the validity of the law of corresponding states in extending the range of values of $\left(\frac{\partial(pv)}{\partial p}\right)_T$ and μ.

To determine the correctness of the first of these assumptions it is simply necessary to plot experimental values of $\left(\frac{\partial(pv)}{\partial p}\right)_T$ against $1/T$. This has been done[19] for hydrogen, nitrogen, and carbon dioxide from the results of Chappuis, Rayleigh, Leduc,

[19] Keyes, J. Math. Phys. M. I. T., 1, 89, 1922.

* The prime refers to quantities measured on the gas scale.

Leduc and Sacerdot, Schalkwijk, and Jaquerod and Scheurer. In each case a straight line is the most representative one that can be drawn. Thus the form of the function at the pressures used in gas thermometry is

$$\left\{\frac{\partial(pv)}{\partial p}\right\}_T = a + \frac{b}{T}$$

From this it follows

$$pv = \left(a + \frac{b}{T}\right)p + f(T)$$

and, since at very low pressures $pv = f(T) = RT$, we have

$$pv = RT + p\left(a + \frac{b}{T}\right)$$

In the second term p may be replaced by RT/v, giving

$$pv = RT\left(1 + \frac{a}{v}\right) + \frac{Rb}{v}$$

$$= \frac{RTv}{v-a} + \frac{Rb}{v}$$

so that

$$p = \frac{RT}{v-a} + \frac{Rb}{v^2}$$

an equation of the type of (12) at low pressures and showing the pressure to be a linear function of the temperature at constant volume.

Assumption (2), involving the use of the law of corresponding states, is questionable. It has been shown to be invalid on the basis of the experimental data. The equation of state of Keyes indicates that the law is in general only true for monatomic substances and then with certain modifications over the usual form of statement. In the latter case, the values of the critical constants to be taken are not those experimentally measured at the true critical point, but rather the values at the critical point the substance would have if it conformed to its equation of state, right up to the point of condensation. This, in general, is not the case, owing to association of the molecules as the specific volume approaches that of the liquid.

D. Analysis of the Isothermals and Isometrics of Hydrogen

Finally, mention should be made of the investigation of Kamerlingh Onnes and Braak[20] in which corrections for the constant

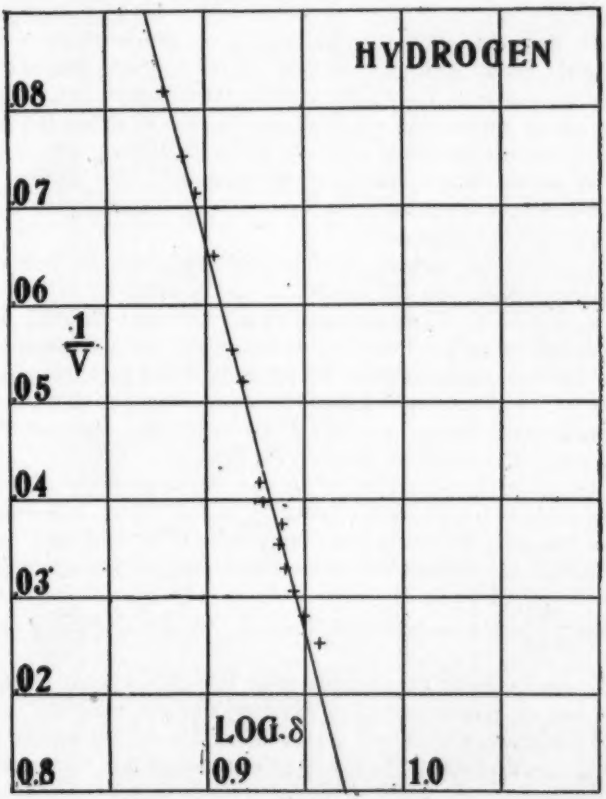

Fig. 2

volume hydrogen thermometer were determined from direct observations of the isotherms of hydrogen. The isotherms were

[20] Onnes and Braak, Leiden Comm. Nos. 97 (1906); 99a, 100a (1907).

here represented as a function of the inverse volume, namely,

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v^2_A} + \frac{D_A}{v^4_A} + \frac{E_A}{v^6_A} + \frac{F_A}{v^8_A} + \ldots$$

where the subscript A denotes values on the absolute scale. Since the actual measurements are referred to the hydrogen constant volume scale, the coefficients first calculated for this expression are an approximation. They can be used to determine provisional corrections to the temperature scale and then, with these, better values for the constants can be found. This method of successive approximations is applied until no change results from a repetition of the process.

In general the number of observations on any one isotherm were no greater than the number of " virial coefficients " chosen to represent it. Complete accordance between observed and calculated values can thus be obtained; but it must be remarked that the final equation embodies whatever errors there may have been in the measurements themselves. It may not happen, for example, that such an equation would be the best representative line that could be drawn through the data.

The constants for hydrogen in the Keyes equation of state were evaluated from data of Amagat and of Onnes and Braak. The Amagat data covered the range from 0° to 200° and from them the δ function could be determined. The relative magnitude of the $\frac{A}{(v-l)^2}$ term is so small here, however, that the constants A and l could not be found at all accurately. For this purpose, recourse was had to measurements at low temperatures, using the value of δ previously determined. In Fig. 2, $\log \delta$ is plotted against $1/v$ for the Amagat data. The points give a straight line, the equation of which is $\log \delta = \log \beta - \alpha/v$. With the δ function determined in this way, we may calculate ϕ, $\left(\frac{A}{(v-l)^2}\right)$, from the data of the observers listed in Fig. 3 and plot the volume against $\frac{1}{\sqrt{\phi}}$ as is

here done. The best representative line is again straight, and from it the constants A and l are determinable. The inconsistency of the various measurements at low temperatures is apparent from the irregularity of the deviations. The equation of state for hydrogen thus takes the form:

$$p=\frac{40.72T}{v-\delta}-\frac{39102}{(v-1.183)^2} \qquad [12a]$$

where

$$\log_{10}\delta=0.9831-\frac{1.26}{v}$$

in gram, atm., c.c. units.

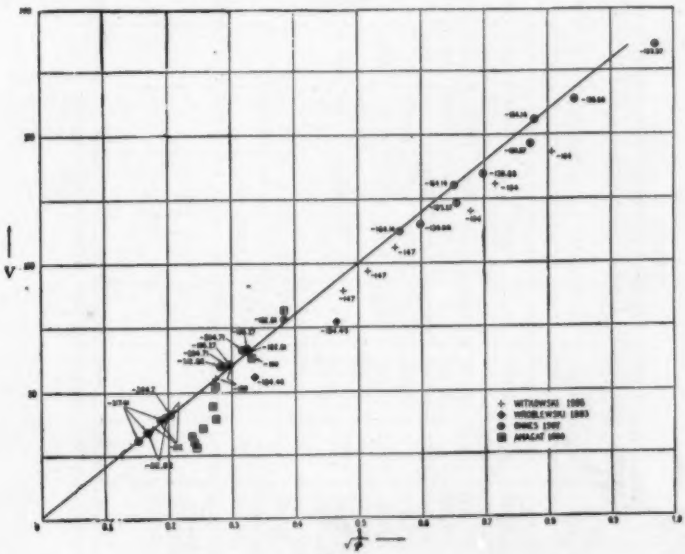

Fig. 3

Tables V and VI give a comparison of the pressures calculated from this equation of state with the observed pressures of Onnes and Braak,[21] Onnes, Crommelin and Miss Smid,[22] and Witkowski.[23] While the deviations are not large, seldom one per cent

[21] Onnes and Braak, Leiden Comm., **100b** (1907).
[22] Onnes, Crommelin and Miss Smid, Leiden Comm., **146b** (1915).
[23] Witkowski, Krak. Anz. **305**, 1905.

TABLE V
Comparison of Observed and Calculated Pressures of Hydrogen
Onnes and Braak[21] Onnes, Crommelin and Miss Smid[22]

−217.40°C (−217.41)		−204.69°C (−204.70)		−183.18°C		−139.88°C		−103.57°C		0.00°C		20.00°C		100.20°C	
V. c.c.	*P.* Atms.	*V.* c.c.	*P.* Atms.	*V.* c.c.	*P.* Atms.	*V.* c.c.	*P.* Atms.	*V.* c.c.	*P.* Atms.	*V.* c.c.	*P.* Atms.	*V.* c.c.	*P.* Atms.	*V.* c.c.	*P* Atms.
768.1	*0.295	7668.	*0.363	177.5	*20.40	216.2	*25.43	7705.	*0.896	413.0	*27.33	190.1	*65.25	497.7	*30.97
	*0.295		0.363		20.54		*25.40		*0.897		*27.39		*64.99		*30.98
142.4	14.64	159.6	16.75	146.5	24.71	163.6	33.77	214.0	32.99	318.6	35.60	170.5	73.08	388.8	39.80
	15.11		17.01		24.87		33.71		32.90		35.58		72.74		39.83
122.5	16.79	129.8	20.46	127.5	28.37	134.6	41.27	178.8	39.66	262.6	43.41	161.6	77.36	3 0	50.25
	17.41		20.78		28.58		41.14		39.54		43.38		76.95		50.30
107.9	18.86	109.7	24.02	111.6	32.42	115.0	48.56	143.2	49.90	226.4	50.58	154.3	81.19		
	19.60		24.46		32.72		48.34		49.66		50.52		80.73		
39.24	46.42	72.66	35.49									147.5	85.13		
	47.83		36.28										84.43		
34.34	52.90	66.47	38.64									142.4	88.38		
	53.36		39.49										87.79		
31.00	58.97	60.29	42.44									136.1	92.68		
	58.00		43.31										91.31		
		41.31	61.92									131.1	96.49		
			61.87										95.76		
												126.4	100.34		
													99.54		

* The observed pressure is given first, that calculated immediately beneath.

TABLE VI
Comparison of Observed and Calculated Pressures of Hydrogen
Witkowski[23]

	−212°C		*−205°C*		*−183°C*		*−147°C*		*−104°C*		*−77°C*		*0°C*		*100°C*	
P. Obs. Atms	*V. c.c.*	*P. Cal. Atms.*	*V. c.c.*	*P. Cal. Atms.*	*V. c.c.*	*P. Cal. Atms.*	*V. c.c.*	*P. Cal. Atms.*	*V. c.c.*	*P. Cal. Atms.*	*V. c.c.*	*P. Cal. Atms.*	*V. c.c.*	*P. Cal. Atms.*	*V. c.c.*	*P. Cal. Atms.*
1	2456	1.01	2747.	1.008	3651.	1.005	5132.	1.001	6882.	1.001	7189.	1.002	11127.	1.000	15200.	1.000
10	238.7	10.16	269.9	10.11	365.2	10.01	515.7	10.00	693.0	9.995	804.3	9.940	1119.	10.08	1527.	10.00
20	114.9	20.55	131.9	20.36	181.9	20.09	259.3	19.53	349.1	19.96	405.1	19.95	563.0	19.97	767.2	19.99
30	74.1	30.95	86.03	30.72	121.2	30.11	173.9	29.91	234.5	29.89	272.1	29.88	377.6	30.01	513.9	29.91
40	54.1	41.32	63.61	40.95	90.91	40.13	131.3	39.72	177.3	39.78	205.6	39.80	284.9	39.89	387.2	39.97
50	42.9	50.90	50.60	50.82	72.90	50.05	105.8	49.63	142.9	49.64	165.7	49.60	229.2	49.82	311.3	49.91
60	35.8	59.83	42.16	60.32	61.09	59.80	89.03	59.34	120.1	59.46	139.1	59.41	192.5	60.55	260.3	59.87

the agreement is not as good as might be wished. In Fig. 4, the deviations of the calculated from the observed pressures are plotted for the Leiden data and those of Witkowski. The former are represented by dotted, and the latter by solid lines. For isotherms from $+100°$ to $-140°$ the deviation increases fairly regularly, the calculated value being too small, and amounting to about one-half of one per cent at 60 atms. At lower temperatures the

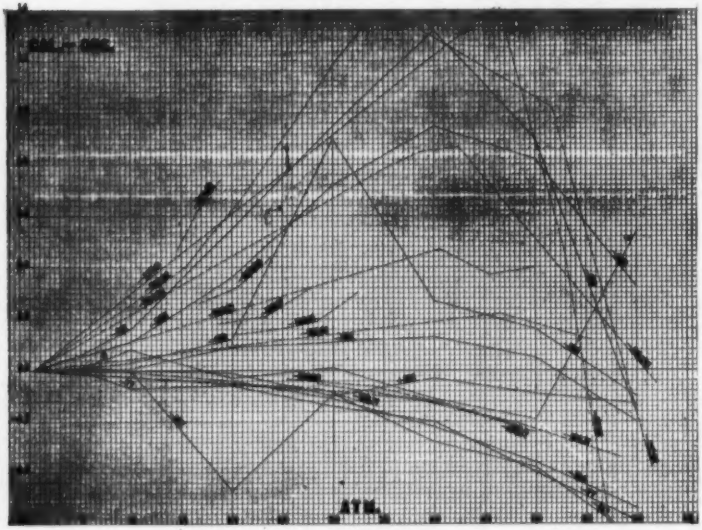

Fig. 4

deviations have the opposite sign and increase to a maximum (ca. 2%) at about 40 atms. and then rapidly decrease. The plot reveals much greater discrepancies in the data than were suspected by the observers. For example, at 20.5 atms. the deviation of the 204.69° isotherm differs from that of the 204.70° isotherm by 0.16 atm. Since these temperatures are the same within the limits of experiment, it follows that the observed pressures, at this particular point, differ by more than 0.5 per cent. Several other

cases will be found as striking. The deviations are too inconsistent to surely indicate a fault in the values calculated by means of the equation of state. This inconsistency is further brought out in a comparison of calculated with observed values at extremely low temperatures. Table VII contains such a comparison, based on

TABLE VII

Comparison of Observed and Calculated Pressures of Hydrogen Onnes and de Haas[24]

−257.26°C		−255.46°C		−252.63°C.	
V. c.c.	*P.* Atms.	*V.* c.c.	*P.* Atms.	*V.* c.c.	*P.* Atms.
9603	0.06698*	6514	0.10964*	2338	0.34786*
	0.06698*		0.10976*		0.36884*
4829	0.13153	3415	0.20672	1315	0.60358
	0.13250		0.20806		0.64848
		2520	0.27759		
			0.28065		
		2225	0.31294		
			0.31707		
		2223	0.31318		
			0.31730		

the data of Onnes and de Haas. Evidently, at temperatures very nearly the same and at the same volumes, the deviations of the calculated from the observed pressures in the various series are very different. Moreover, at such large volumes it seems improbable that the deviation from the perfect gas law is as great as the measurements indicate.

Another, and more direct, method is available for analyzing the data on hydrogen. This consists in determining the isometrics and for this purpose the pressures† have been calculated for a number of fixed volumes from the isothermal equations of Onnes. The isometrics so calculated are presented in Table VIII and Fig. 5. In each case a straight line seems best to represent the data. If we denote the equation of an isometric by

$$p = \psi T - \phi$$

the values of ψ and ϕ obtained from the lines of Fig. 5 are given in Table IX.

* The observed pressure is given first, that calculated immediately beneath.
†Pressures in atmospheres.
[24] Onnes and de Haas, Leiden Comm., **127c**, 1912.

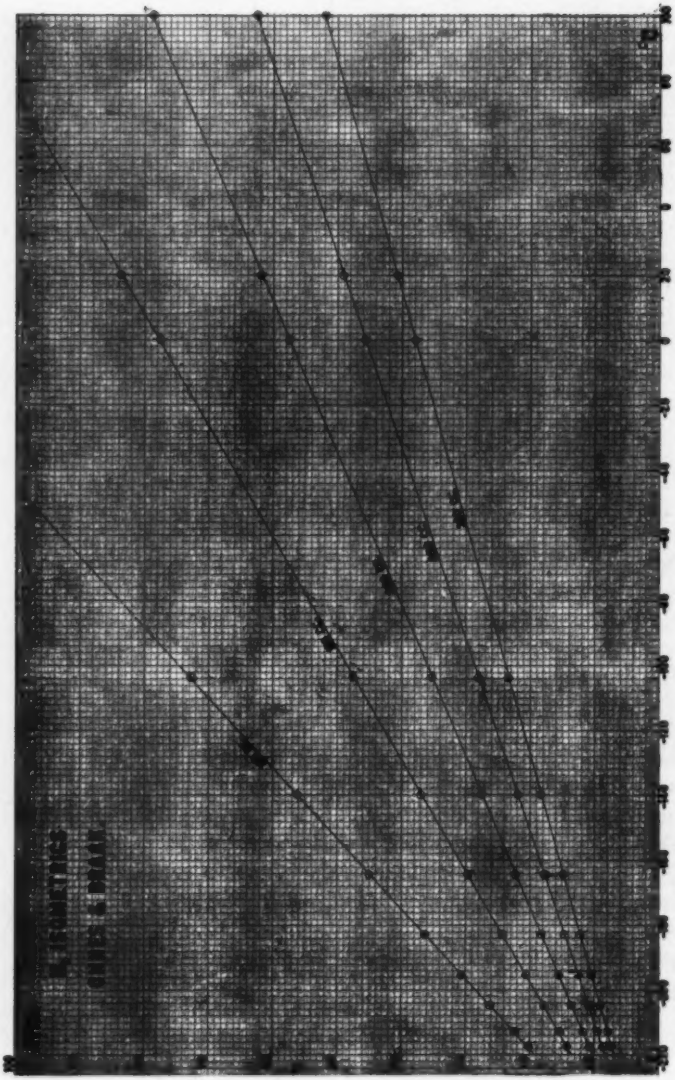

Fig. 5

TABLE VIII

H_2 Isometrics. Onnes and Braak,[21] Onnes, Crommelin, and Miss Smid[22]

t°C	*100 c.c.*	*150 c.c.*	*200 c.c.*	*250 c.c.*	*300 c.c.*
−217.41	20.169	14.216	10.659	8.631	7.252
−212.82	22.324	15.309	11.663	9.432	7.906
−204.70	26.212	17.776	13.465	10.841	9.074
−195.27	30.622	20.588	15.526	12.466	10.415
−182.81	36.329	24.235	18.205	14.585	12.167
−164.14	45.032	29.744	22.275	17.805	14.818
−139.88	56.179	36.933	27.531	21.949	18.251
−103.57	72.767	47.561	35.348	28.131	23.363
0.00		77.544	57.471	45.657	37.873
20.00		83.662	61.896	49.127	40.730
100.20			78.743	62.537	57.863

Fig. 6a exhibits the deviations of the observed pressures from those calculated from the constants of the isometric equations presented in Table IX. It will be seen that the most representative line has been chosen in each case. The conclusion that the pressure is a linear function of the temperature at constant volume is

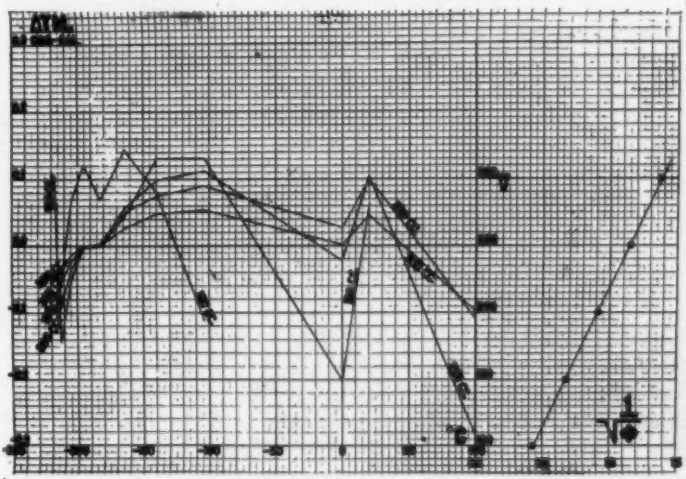

Fig. 6a

Fig. 6b

TABLE IX

Constants of the Isometrics of Hydrogen

100 c.c.		*150 c.c.*		*200 c.c.*		*250 c.c.*		*300 c.c.*	
Ψ	Φ	Ψ	Φ	Ψ	Φ	Ψ	Φ	Ψ	Φ
0.46213	5.480	0.29270	2.200	0.21491	1.205	0.16983	0.756	0.14061	0.533

consequently at least not disproved, but supported, as far as the accuracy of the data are concerned. It thus becomes difficult to perceive how corrections to the constant volume hydrogen thermometer, deduced from the virial equation based on the same data, can represent a true fact of nature.

The constants of the equation of state can be found from the above isometrics for

$$\frac{R}{v-\delta}=\psi$$

and

$$\frac{A}{(v-l)^2}=\phi$$

The values of δ derived from the above isometrics are given below, compared with the corresponding values of δ calculated from the equation of state (12a). The variation of δ is too small to be

TABLE X

Values of δ

	100 c.c.	*150 c.c.*	*200 c.c.*	*250 c.c.*	*300 c.c.*
From Ψ	11.88	10.88	10.52	10.19	10.39
From Equa. 12*a*	9.34	9.34	9.48	9.51	9.53

detected within the limits of precision of the measurements, while the discrepancy between the two sets of values corresponds to an error in the volume of about 0.5 per cent, which is possible in view of discrepancies already indicated.

The volume plotted against $\frac{1}{\sqrt{\phi}}$ should give a straight line,

from the constants of which A and l can be determined. This plot is represented in Fig. 6b. The values of A and l from the line there drawn are

$$A=43600 \quad l=10.2$$

Based entirely upon the Leiden data, the equation of state for hydrogen becomes

$$p=\frac{40.72T}{v-10.5}-\frac{43600}{(v-10.2)^2}$$

These constants, it is believed, may not be as reliable as those previously accepted for hydrogen. The coefficients of expansion and pressure increase of the gas will not, however, be appreciably altered if calculated with the new constants; but the corrections to the constant pressure hydrogen thermometer will differ from those computed by Buckingham from the Joule-Thomson data. The equation of state for hydrogen cannot be considered definitely established, but until more accurate data are available, equation (12a), given on page 263, can be regarded as best representing the facts.

A critical test of the validity of form of the equation of state, (12a), as well as of its constants, is obtained by calculating the Joule-Thomson coefficients of hydrogen and the inversion temperatures of the Joule-Thomson effect. These can then be compared with the values calculated by J. P. Dalton[25] from the hydrogen virial coefficients of Onnes.

The Joule-Thomson coefficient is defined by the equation

$$\mu=\frac{T\left(\frac{\partial v}{\partial T}\right)_p-v}{C_p}$$

while from the equation of state

$$\left(\frac{\partial v}{\partial T}\right)_p=\frac{(v-\delta)}{T}\left[\frac{1}{1-\frac{2A}{RT}\frac{(v-\delta)^2}{(v-l)^3}-\frac{a\delta}{v^2}}\right]$$

[25] Dalton, Leiden Comm., **109a** (1909).

also $$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-\delta}$$

and

$$Cp = Cv + T\left(\frac{\partial p}{\partial T}\right)_v \cdot \left(\frac{\partial v}{\partial T}\right)_p = C_v + R\left[\frac{1}{1-\frac{2A}{RT}\frac{(v-\delta)^2}{(v-l)^3}-\frac{a\delta}{v^2}}\right]$$

and finally

$$\mu = \frac{\frac{2A}{RT}\cdot\frac{v(v-\delta)^2}{(v-l)^3}-\delta\left(1-\frac{a}{v}\right)}{Cv\left[1-\frac{2A}{RT}\cdot\frac{(v-\delta)^2}{(v-l)^3}-\frac{a\delta}{v^2}\right]+R} \tag{13}$$

For values of μ at low pressures (13) reduced to

$$\mu = \frac{2A}{C_p RT}-\frac{\beta}{C_p} \tag{13a}$$

The inversion temperature, corresponding at $\mu = 0$.

$$T_i = \frac{\frac{2A}{R}\cdot\frac{v(v-\delta)^2}{(v-l)^3}}{\delta(1-a/v)} \tag{14}$$

TABLE XI
Joule-Thomson Coefficient for Hydrogen at 1 Atm.

T °C	μ *from [13a]* °C *per Atm.*	μ, *Dalton* [25] °C *per Atm.*
−215	+0.167	+0.291
−186	+0.088	+0.141
−157	+0.049	+0.073
−128	+0.026	+0.037
−99	+0.010	+0.015
−84.5	+0.004	+0.006
−70	−0.001	−0.001
−41	−0.010	−0.011
−12	−0.016	−0.019
+17	−0.021	−0.026

TABLE XII
Inversion Temperature of Joule-Thomson Effect for Hydrogen

Pressure Atms.	T_i, *from [14]* °C	T_i, *Dalton* [25] °C
1	−73.2	−72.6
10	−75.9	−74.1
20	−78.3	−75.8
50	−85.7	−81.9
100	−99.0	−91.7

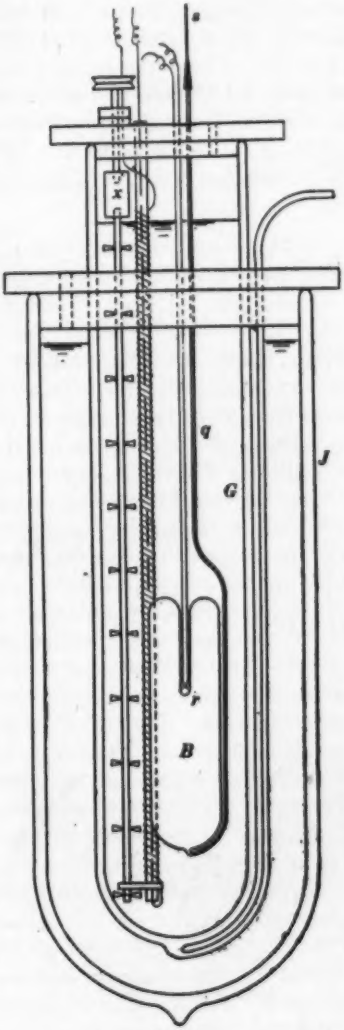

Fig. 7

A comparison of values computed fron (13a) and (14) with those found by Dalton is given in Tables XI and XII. In calculating μ, C_p has been assumed to have the constant value 3.41 cal. per gram, as was accepted by Dalton, in order to make the results comparable. In view of the rather involved computations by means of the virial equations the agreement may be considered satisfactory and lends support to the mathematical form of the equation of state.

IV. Description of the Apparatus

The Bulb

The bulb B (Fig. 7) is of fused quartz, 135 mm. long and 33 mm outside diameter. The thickness of the walls is approximately 0.75 mm. During the earlier experiments a reëntrant tube r, about 3 mm. in diameter and 45 mm. long was provided at the top of the bulb to receive a thermocouple. The bottom of this tube was finally fractured, owing to the freezing of a small amount of water which condensed therein on standing over from a previous experiment. In repairing the bulb the reëntrant tube was removed, as it had not been found altogether satisfactory. The volume of the first form, with reëntrant tube, was 91.31 c.c. at room temperature. The volume of the present bulb is 91.86 c.c. At the bottom of the bulb there is fused a quartz capillary, q, fashioned in the manner shown, which extends above the top of the vessel containing the bath. The end of the quartz capillary is ground into a conical steel cap and cemented with de Khotinsky cement. A silver capillary is soldered into the upper end of this cap and serves to connect the bulb with the manometer. The length of the quartz capillary is 50 cm. and its volume 0.00316 c.c. per cm. The bulb is supported by means of a quartz rod, Q (Fig. 12), fused to its top and which is cemented into a brass collar screwed to the cryostat cover.

The choice of fused quartz as bulb material rests mainly upon its small coefficient of thermal expansion and its supposedly less tendency to adsorb gases. If glass were used, its thermal expansion would have to be known very accurately. The values of the

coefficient of expansion of quartz were taken from an analysis of the existing data by R. S. Taylor and L. B. Smith[26] of this laboratory.

The following relation was used for the true linear temperature coefficient of expansion, λ, of quartz below 0°C.:

$$\log_{10}(\lambda \times 10^7 + 19) = 1.5414 - \frac{50.789}{T}$$

Quartz exhibits a maximum density at about −80°C. and its mean coefficient of expansion passes through zero at −148°C. This property makes it especially desirable as a thermometric gas container at low temperatures.

The change in volume of the bulb with pressure was determined as follows. The bulb and a portion of the quartz capillary were filled with water and placed in a horizontal position. The capillary was then connected through a three-way stopcock to a vertical tube and the latter partly filled with mercury, the lower end of the mercury being in contact with the surface of the water in the capillary. The length of the mercury column was then increased, and the displacement of the contact surface between the mercury and water noted. The volume per unit length of the capillary being known, the change of volume with pressure could be determined after making a correction for the compressibility of the water. By means of the three-way stopcock, the excess of mercury could be drained from the apparatus and the experiment repeated. The mean of four such measurements gave the pressure coefficient of the bulb as .0110 c.c. per atm. ± 0.0003. The figure given by Chappuis[27] for the quartz bulb used by him is 0.00444 c.c. per atm., reduced to the same volume. It is probable that th difference is due to the thinner walls of the thermometer bulb.

[26] This will be published in a forthcoming paper on the density and vapor pressure of ether at low temperatures. The papers consulted in connection with the thermal expansion were:
Holborn and Henning, Ann. der Phys. **10**, p. 446, 1903.
Scheel and Chappuis, Wiss. Abh. Phys. Tech. Reichsanstalt, **4**, p. 54, 1904.
Harlow, Proc. Roy. Soc. Lond., **24**, p. 30, 1912.
Henning, Ann. der Phys. **22**, p. 606, 1907.
Scheel and Dorsey, Phys. Rev. **27**, p. 101, 1907.
Randall, Phys. Rev., **3a**, p. 216, 1910.

[27] Chappuis, Trav. Men. Bur. Inst., **6**, 1888.

The Connecting Capillary

The internal diameter of the silver capillary, connecting the bulb with the manometer, was determined from measurements of its length, weight, and external diameter: the density of the silver being taken as 10.5. The internal diameter thus found was 0.457 mm. The length of this connection is 144 cm. and its volume consequently 0.00164 c.c. per cm.

The lower end of the silver capillary connects with a capillary of glass, g (Fig. 8), 15 cm. long, which is cemented into the steel cap, k, of the short manometer tube. The introduction of this glass capillary is a safeguard to prevent mercury from reaching the silver tube should the level inadvertently be raised above the contact point. It served this purpose on two occasions.* The volume of the glass section was found to be 0.296 c.c.

The Manometer

The manometer tubes, C and C' (Fig. 8), are of pyrex glass specially selected for uniformity of bore and straightness, their internal diameter being 15 mm.† The tubes are fastened into the wells of the manometer base D through rubber stoppers forced tight by means of the brass clamps d. The long tube is supported near the top by a centering device on the cover plate of the manometer frame A. The under side of the short tube cap k is provided with a steel needle point 0.3 mm. long. This detail is shown in the enlargement. Exact contact between the point and the mercury meniscus is determined by placing the gap in series with a small electromagnetic interrupter and telephone receiver. The long tube is connected to a vaccum pump and maintained exhausted, so that the indications are independent of barometric pressure.

The manometer base D is of steel $20\times10\times10$ cm. It is screwed to a steel leveling stand L (Fig. 10), the whole resting on two massive blocks of slate. The manometer tubes are connected by a

* A small valve could of course be used instead; but this seemed an unnecessary complication and one almost surely destined to provide trouble.

† The tubes were calibrated for bore and the correction for capillary depression was found to be negligible.

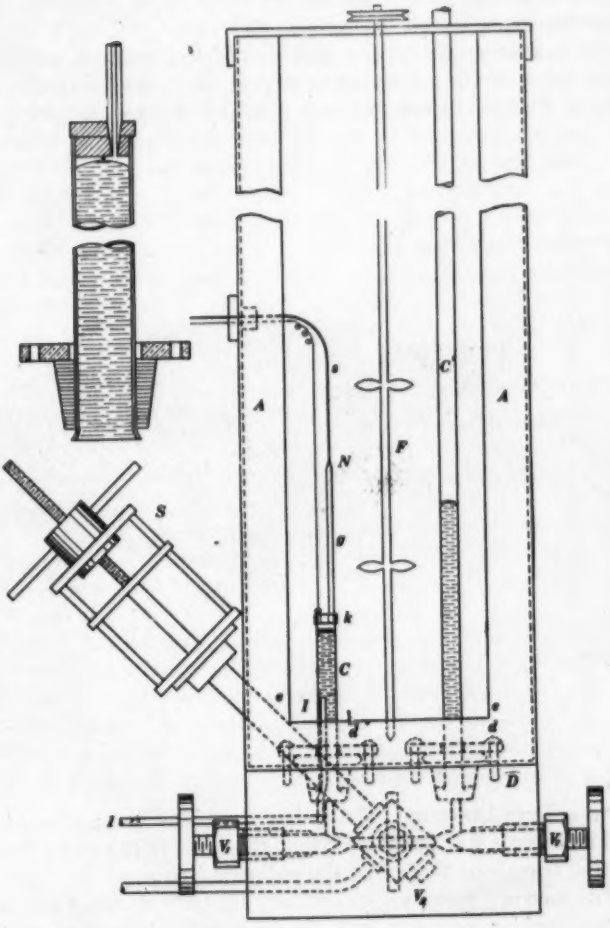

Fig. 8

passage 1.6 mm. in diameter. A second passage at right angles to the first and half way between the tubes makes connection with the mercury reservoir.

Each manometer tube is provided with a shut-off valve V_1. The valve details are shown in Fig. 9. In closing the valve the piston P moves forward without rotation, thereby preserving the

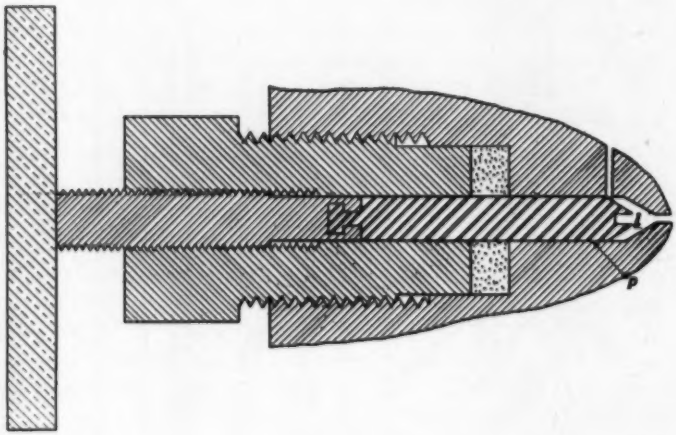

Fig. 9

packing from loosening. The end of the piston is cup-shaped, l, and its taper is 0.5° less than that of the seat. In this way a firmer seating is realized than with the ordinary form.

The mercury reservoir, an ordinary lift-bulb mounted between vertical guides, connects with the manometer base through the rubber pressure tubing R (Fig. 8) and the shut-off valve V_2. The steel block containing this valve is threaded into the base

and made tight with an aluminum washer. The reservoir is used only for rough adjustment of the mercury level. The valve V_2 is then closed and fine adjustment made by means of the injector S. One turn of the handle raises the level of the mercury in the short tube about 0.04 mm.

The frame A of the manometer is fashioned from an iron channel section. The section was cut at the corners *ee*, bent into a U form and the corners welded. The bottom and faces were planed smooth. It is fastened to the base by screws and made tight by an impregnated paper gasket. Sheets of plate glass are screwed to front and back. These faces were made water-tight with heavy shellac and the outer edges sealed with litharge and glycerin cement. A stirrer, F, provides circulation of the bath liquid, the temperature of which is given by a calibrated Baudin thermometer t (Fig. 10) graduated to 0.1°C.

Kerosene was used as a bath liquid during the greater part of the measurements. The rubber stoppers seating the manometer tubes were covered with a thick layer of shellac to prevent their disintegration. After more than a year's use the kerosene finally reached the stoppers and they had to be replaced. Thereafter water was used instead of kerosene. The interior surfaces of the frame and the base were covered with red lead paint to prevent rusting and then painted white to improve the illumination of the columns.

Gas is admitted to the bulb through the tube I (Fig. 8). The mercury is allowed to fall below the upper end of I, the tube now remaining filled with mercury back to the stopcock 1 (Fig. 10). This is drained out into the trap T. When the bulb has been loaded the mercury is allowed to ascend in the short manometer tube and the inlet tube is again filled with mercury back to 1.

The Cathetometer

The difference in level of the fixed point and the column in the long tube was measured with a Gaertner cathetometer. This instrument possesses a steel scale which was compared with a Gaertner standard meter (No. 1768) calibrated by the Bureau of Standards. The scale error was found sensibly constant and

amounted to 0.00002 cm. per cm. Taking the coefficient of expansion of steel to be 11×10^{-6}, the scale correction is given by the following formula:

$$H_{cor.} = H_{obs.}[1+11\times10^{-6}(t-20)+20\times10^{-6}]$$

The instrument is fitted with a micrometer screw attachment by which 0.01 mm. can be read and 0.001 mm. estimated. With practice it was found that successive readings deviated by not more than a few thousandths of a millimeter.

The Cryostat

The thermometer bulb is mounted in the form of cryostat shown in Fig. 7. The inner vessel G, containing the bath, is of pyrex glass and double-walled. The space between the walls is connected to the vacuum pump and can be exhausted to any desired degree. The length of this vessel is 40 cm. and its internal diameter 6.7 cm. It is closed by a cover of asbestos wood. To this cover are attached a heater and a stirrer; the resistance wire of the heater being wound on a glass rod with asbestos string insulation between the windings. To minimize heat conduction a vulcanite section x is placed in the stirrer shaft just beneath the cover. The bath vessel is cemented with de Khotinsky cement into the asbestos wood cover of the outer Dewar tube J. This latter is 40 cm. long with an internal diameter of 13.5 cm. The outer vessel, and also its cover, bearing the inner vessel, are mounted in vertical guides between the surfaces of a double-decked table. For the bath liquid normal pentane was used, which remains quite liquid down to -145°C. For comparisons below this point the thermometer was immersed directly in liquid air or oxygen.

The outer vessel being filled with liquid air, maintained at a fairly constant level, the temperature of the bath can readily be held constant at any desired point by suitably regulating the heating current and the degree of exhaustion within the walls of the bath vessel. In practice, the walls are pumped out to the right degree as determined by experiment and the temperature control during the observations effected solely by hand regulation of the heater current. Over a period of fifteen or twenty minutes the temperature can be held to the same value within 0.01°C.

Auxiliary Apparatus

Fig. 10 illustrates the general arrangement of the apparatus. *M* represents a supply of helium, *K*, a hydrogen generator, and when nitrogen was used it was introduced at *E*. A Toepler pump

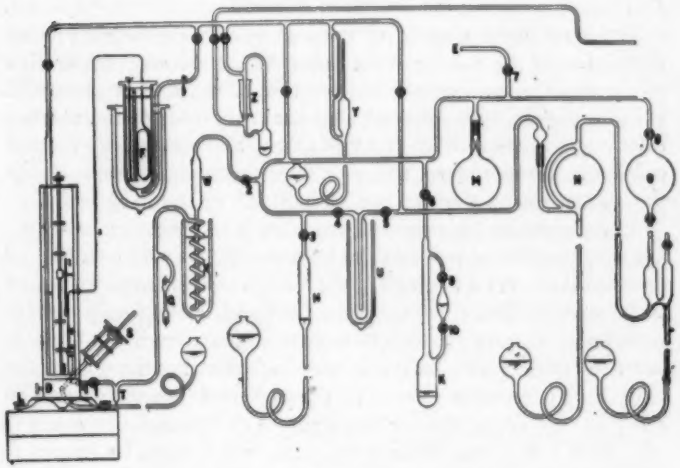

Fig. 10

N served to transfer the helium from its container to the gas reservoir *O*. In the cases of hydrogen and nitrogen, where fresh gas could be generated whenever needed, the Toepler pump was not used, the reservoir being filled directly from the generator. *U* is a carbon adsorbing tube to be immersed in liquid air in purifying the helium. The gas could be circulated repeatedly through the purifying tube by means of the pump. *H* is an auxiliary lift pump for convenience in loading the thermometer. Before entering the bulb the gas passed through the purifying tube *W* containing soda lime and phosphorus pentoxide and the

spiral X immersed in liquid air. A Geissler tube Q served as means of checking the purity of the gas. At Y and Z are shown a McLeod gauge and mercury diffusion pump. The latter is backed up by a rotary oil pump capable of giving 0.01 mm. With the two in series the apparatus could be exhausted to better than 1×10^{-5} mm.

V. Sources of Error

The three main sources of error in gas thermometry involve the control of the volume of the bulb, the volume and temperature of the dead space, and the temperature of the mercury columns. For the present it is assumed that the total mass of the thermometric gas exists only in the gas phase, and we reserve for discussion in another place, the error which may result from adsorption of the gas on the walls of the bulb at low temperatures.

Assuming that it is desired to measure a temperature of $-100°$ C., it is possible to forecast the accuracy with which this can be accomplished. The actually observed pressure can be measured to 0.01 mm. The corrections for temperature expansion of the cathetometer scale and the reduction of the mercury column to standard gravity can be made with sufficient accuracy to introduce no appreciable error. If the recorded pressure is about 500 mm. the correction for temperature of the mercury columns (ca. 25°C.) is of the order of 2.5 mm., which must be known to 0.2 per cent and the coefficient of expansion of mercury together with the mean temperature of the manometer must each be known to 0.14 per cent. Use was made of the coefficient of expansion of mercury given by Callendar and Moss.[28] The mean temperature of the manometer must then be known to ±0.03°C. The necessity of jacketing the columns, therefore, is apparent. The usual procedure of placing two or three thermometers along the column in air is believed to be inadequate. With the columns immersed in a stirred bath of kerosene or water, the temperature of which is given by a calibrated thermometer readable to 0.01°C., we feel hat the necessary condition of determining the average temperature to 0.03° is certainly fulfilled. The correction for difference in

[28] Callendar and Moss, Phil. Trans., 1911. $a = 0.000180555 + 0.0_5 1244t + 0.0_6 254t^2$.

level of the bulb and contact point only amounts to one or two hundredths of a millimeter and can be accurately applied. The dead space correction at the ice point amounts to about 0.04 mm. and at -100°C. to 1.5 mm. This correction should then be known to 0.2 per cent in order to introduce no further error. It follows that the temperature of the dead space should be known to ± 0.1°C. and its volume to 0.14 per cent. Both these conditions can be realized. Thus the pressures, p_o and p, can be determined in the case under consideration to 0.01 mm. or about 1/50,000.

The correction term for change in volume of the bulb must be accurate to about ten per cent in the case of fused quartz, if the precision previously laid down is to be maintained. If a glass bulb is used, the necessary precision of this term would be of the order of one per cent, which for glass would be very difficult to realize and much uncertainty has undoubtedly been introduced into gas thermometry because of the uncertainty of the expansion data. In the case of quartz, both the thermal expansion and that due to pressure can be determined easily with the necessary precision. It thus appears that the bracketed term of the temperature formula (3) can be determined to 1/20,000 under the conditions assumed.

We now have the temperature given as the product of three factors, $\frac{t}{\epsilon_o}$, p_o, and the bracketed term. The estimated precision of these three quantities is 1/12,000, 1/60,000, and 1/20,000 respectively. The percentage error in the temperature can thus be put at 0.01 per cent. Hence, at -100°C. the temperature is determinable to ± 0.01°C. At the boiling point of oxygen, we believe the limit of our present accuracy to be ± 0.02°C.

VI. Description of the Experiments

A. Indirect Determination of the Dead Space Volume

The volume of the dead space could be directly measured with the exception of that part comprised between the level of the contact point and the mercury meniscus. This cannot be sufficiently accurately calculated on the assumption that the meniscus is a segment of a sphere. Moreover, the ellipsoidal formula used

by Travers, Senter and Jaquerod[29] is not in agreement with that used by Chappuis,[27] based on the work of Desains. These two formulæ applied to our case and comprising the volume between the under surface of the steel cap k and the meniscus gave 0.159 c.c. and 0.175 c.c. respectively. Since the more recent measurements of Scheel and Heuse[30] upon meniscus volumes were not known at the time, it was decided to determine the volume experimentally by an indirect method.

Assuming the coefficient of pressure increase of air to be given correctly by calculation from the equation of state, the volume of the dead space could be found after determining the ice and steam points on the gas thermometer; since it would then be the only unknown quantity. A description of the procedure in determining ice and steam points will be given in the next section. It will suffice here to record the dead space volume thus found. On taking the contact space volume to be 0.196 c.c., we have the following measurements of the coefficient of pressure increase of air:

${}^{100}_{0}\epsilon_p$	Air. $p=607.88$ mm.
	Date
0.0036682	1/21/21
0.0036691	1/24/21
0.0036689	1/29/21
0.0036687 $\pm$ 0.0$_n$3 mean.	

The value calculated from the equation of state is 0.0036690.* Subsequently, the experimental results of Scheel and Heuse have come to light and applying these data to the dimensions of the contact space there is found 0.197 c.c. The agreement is astonishingly close in view of the involved manner in which the volume 0.196 was deduced and furnishes evidence of the accuracy of the apparatus and procedure.

The total volume of the dead space is 0.886 c.c. The ratio of dead space to bulb is thus 0.0097. This is larger than might be

* ${}^{100}_{0}\epsilon_p = 0.00366118 + 129 \times 10^{-10} p$, (mm.)

[29] Travers, Senter and Jaquerod, Phil. Trans. **200**, p. 110, 1903.
[30] Scheel and Heuse, Ann. der Phys., **33**, p. 291, 1910.

desired; but inasmuch as 60 per cent of the dead space is within the manometer, where its temperature is accurately known, the dead space correction, though fairly large, is calculable with considerable exactness.

B. Coefficient of Pressure Increase of Nitrogen

As a test of the operation of the apparatus and of the value determined for the dead space volume, $\epsilon_{\circ}^{100}$ for nitrogen was next determined. This could be then compared with the value calculated from the equation of state.

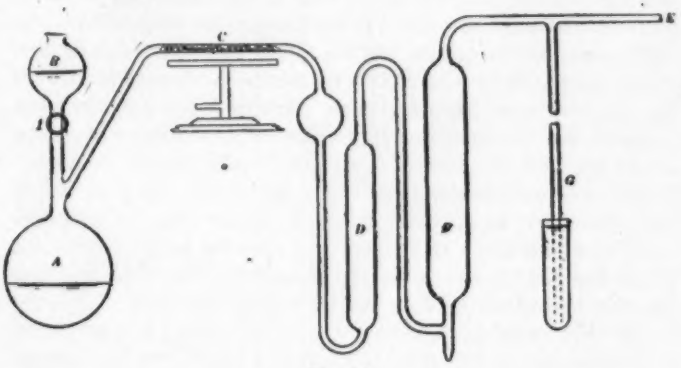

Fig. 11

The nitrogen was prepared in the usual manner by the interaction of ammonium sulphate and sodium nitrite. The generating train is shown in Fig. 11. A solution of 70 grams of NH_4SO_4 in 120 c.c. of water was placed in *A*. *B* contained a solution of 40 grams of $NaNO_2$ in 50 c.c. of water. The nitrite could be admitted gradually into *A* through the stopcock 1, the vessel *A* being warmed in a water bath. The reaction is autocatalytic, and if the temperature is not controlled, proceeds with too great rapidity. The gas passed over heated copper in the quartz tube *C* and then through sulphuric acid in *D* and phosphorus pentoxide in *F*. The tube *G*, dipping into mercury, acted as a safety valve. The gen-

erating train was connected to the rest of the system at E (Fig. 10). Before preparing the gas the whole system was pumped out and repeated rinsing with the gas preceded the final exhaustion and filling of the reservoir O. The pressure within the reservoir could be read by means of the mercury column J.

The reservoir having been filled with nitrogen at about one atmosphere pressure, the generating train was now shut off at 7 and the rest of the system completely exhausted. Stopcocks 4 and 5 were kept closed, the carbon purifying tube being used only in the case of helium. By lowering the mercury in the short manometer tube below the gas inlet and allowing the mercury in the inlet passage to flow into the trap T, the bulb could be placed in communication with the pump through the stopcock 2. The bulb was maintained at 360°C. within an electric heater and exhausted to 0.0001 mm. at this temperature. A small amount of gas was now introduced and after standing a few minutes again pumped out. This rinsing process was repeated four or five times before the bulb was allowed to cool and finally loaded. In adjusting the pressure to the desired amount the lift pump H was of use. Gas could be admitted into H from the reservoir and then after closing 8 could be pushed over into the bulb. During the filling the coil X was cooled by liquid air to remove any condensible constituents. Examination of the spectrum of the gas in the Geissler tube Q furnished satisfactory evidence of its purity.

To determine the ice point the bulb was placed in a large Dewar tube and surrounded with shavings of distilled water ice. Ice cold distilled water was added, immersing the bulb to a depth of two or three inches. The dead space volume was considered in two parts — one at the temperature of the manometer; the other, comprised between the top of the bath and the cover, at the mean temperature of room and bath. In reading the pressure four observations of the height of the fixed point* and of the mercury in the long column were taken. During any run the maximum deviation was not greater than 0.01 mm. The ice points before and after the steam points were found to be:

* The fixed point did not vary during any given run; but its height was found to depend slightly upon the pressure of the gas, due presumably to a small amount of give in the rubber seating of the tube.

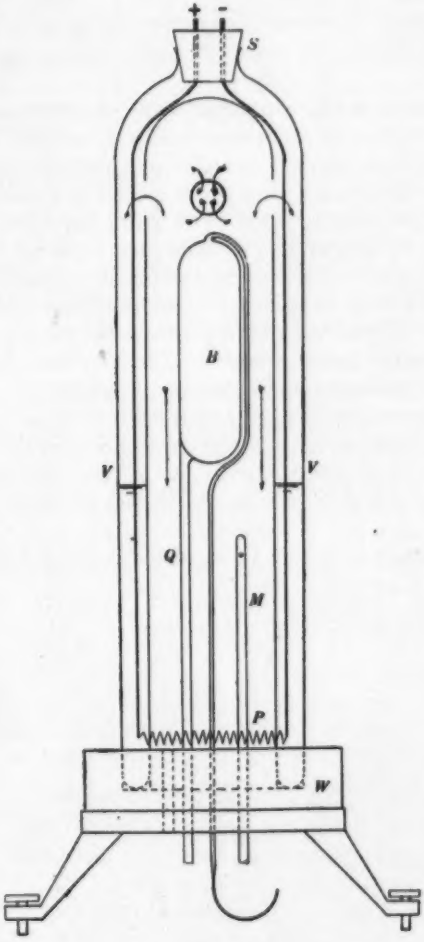

Fig. 12

Ice Point, N_2	
mm.	*Date*
653.80	3/18/21
653.82	4/20/21

The steam point was determined in a specially designed boiler, illustrated in Fig. 12. The double-walled vessel V is of pyrex glass, 40 cm. long and 6.7 cm. internal diameter. Distilled water is placed in the annular space and is heated by a platinum coil P immersed directly in the liquid. The Monel lead wires are brought out through the stopper S. The steam passes through the openings A and down over the bulb, issuing through an opening in the asbestos wood base W. The whole is mounted on a brass leveling stand. A glass tube M connects with a U-tube water manometer to indicate the excess of steam pressure over atmospheric. When in use, a pipe cover is slipped down over the vessel for insulation. This type of boiler was found to give excellent results, the water boiling gently and continuously and the steam pressure not more than one millimeter of water above that of the atmosphere. The readings were found independent of the rate of boiling within wide limits.

Three steam points were taken with the nitrogen filling as follows:

Steam Point, N_2	*Temperature*	
mm.	*°C.*	*Date*
895.06	100.62	3/23/21
894.91	100.57	3/23/21
894.39	100.34	3/24/21

The values for $\epsilon_{0,p}^{100}$ from the mean of the ice points and each steam point are given in the first column of Table XIII. The value calculated from the equation of state* and that given by Henning and Heuse[31] are also given for comparison.

The difference between our measured value and that calculated from the equation of state amounts to 1/7350. The calculated

* For N_2: $=0.00366118+121\times10^{-10}p_0$ (mm.).

[31] Henning and Heuse, Zeit. f. Phys., **5**, p. 285, 1921.

TABLE XIII
Coefficient of Pressure Increase for Nitrogen
$p_o = 653.81$

Measured $\times 10^7$	*Calc., Keyes** $\times 10^7$	*Measured, Henning and Heuse* **31** $\times 10^7$
36698 36693 36698 36696 mean.	36691	36692

value we believe the more nearly correct, especially in view of its agreement with the measurements of Henning and Heuse. It was proposed in measuring temperatures to utilize the calculated values of the coefficients and the above measurements were a test of the sufficiency of the apparatus. We believe that in general a precision of 1/10,000 is realizable.

C. The Diffusion of Helium and Hydrogen Through Quartz

It was originally contemplated to use helium as thermometric gas. To this end the helium in the globe *M* (Fig. 10) — furnished in a high state of purity by the Linde Air Products Co. of Buffalo — was transferred to the reservoir *O*, being circulated repeatedly through the charcoal tube *U* immersed in liquid air. The thermometer bulb was loaded to an ice-point pressure of about 621 mm.

As soon as measurements were undertaken it became apparent that gas was being lost from the bulb. In two days the ice point dropped from 620.74 mm. to 619.29 mm., the bulb remaining at about 27°C. during the interval. The pressure inside being less than atmospheric, the possibility of leakage was excluded. It was known that helium diffuses readily through quartz at high temperatures[32], but such a large effect at ordinary temperatures had not been suspected. The rate of diffusion at 27°C. and 682 mm. internal pressure was found to be 0.03 mm. per hour. At 100°C. the rate appeared nearly ten times as great. Subsequently we have read of a similar experience of Henning,[33] who found the rate of diffusion at room temperature and 700 mm. internal pressure to be 0.01 mm. per hour in the case of the bulb used by him.

[32] Jaquerod and Perrot, C. r., **139**, p. 789, 1904.
[33] Henning, Zeit. f. Phys., **5**, p. 264, 1921.
* For N_2: $=0.00366118+121\times10^{-10}p_o$(mm.).

On account of the rapid decrease in the rate of diffusion with lowering of the temperature it seems probable that it would become negligible at 0°C. If the bulb of the thermometer were not heated above this point it might be possible to utilize the attractive combination of helium in quartz for the measurement of low temperatures; but owing to the difficulties of this procedure the use of helium in the present instance was discarded.

Hydrogen was the next choice. It was prepared by the action of pure sodium amalgam upon water in the type of generator shown at *K* (Fig. 10). The small bulb in the side tube contained air-free water which could be admitted at will into the lower bulb containing the amalgam. The hydrogen was dried in the process of loading by passing through the pentoxide tube *W* and the spiral *X*.

Diffusion of the gas through the walls of the bulb was again found, although to a much less extent than in the case of helium. The ice-point pressure of the initial loading was 645.11 mm. A succession of steam points gave lower pressures each time, the drop amounting to 0.4 mm. in four days. An estimate of the rate of diffusion at any definite temperature cannot be given, it being only possible to conclude that at 100°C. it is considerably greater than 0.004 mm. per hour.

The possibility of using hydrogen in quartz is by no means excluded, although the rate of diffusion at 100° is large enough to cause some difficulty in determining the coefficient of pressure increase. It had been decided, however, to employ nitrogen also in the investigation and with this gas diffusion causes no trouble. Later a comparison was made with the hydrogen thermometer.

D. Measurements with the Nitrogen Thermometer

Thermocouple Calibration

With the nitrogen thermometer a calibration was made of a multiple copper-constantan thermocouple down to the boiling point of oxygen. The thermocouple consisted of six copper-constantan couples in series, each wire of No. 30 B. & S. gauge. The junctions were silver soldered by bringing a tiny drop of molten silver solder into contact with the junction, thus avoid-

ing direct heating of the wires with the blow pipe flame. Each lead was covered with bakelite varnish and baked at 100°C. for several hours. They were further insulated from each other with silk floss and then tied together with silk thread to form a pencil three millimeters in diameter and five centimeters long. The "cold junction" was kept in ice within a small thermos bottle. The "hot junction" could be introduced into the reëntrant tube of the thermometer bulb. With this arrangement there seemed no doubt that the temperature of the indicating junction and that of the gas within the bulb would be the same.

The electromotive force of the thermocouple was measured on a Leeds and Northrup Type K potentiometer in conjunction with a high sensibility galvanometer of seventeen ohms internal resistance. The whole electrical system was placed on interconnected metal plates in order to be shielded from surface leakage due to external potential differences.[34] Very little trouble was experienced from leakage effects except during one period of extremely damp weather when measurements had to be suspended. The indications of the thermocouple were reproducible to one microvolt.

The first calibration was made at twelve temperatures ranging from −18.33°C. to −183.39°C. on the nitrogen scale. A check calibration at −183.15°C. was made two months later, and after a further period of three months, another calibration was undertaken in the range −51.12°C. to −130.54°C. This latter calibration furnished a very good check on the reliability of the gas thermometer and the constancy of the thermocouple, for it was made under quite different conditions. The quartz thermometer bulb had been broken during the intervening period and in its new form was without the reëntrant tube. The individual junctions of the thermocouple had, moreover, been separated and each protected by a thin tube of glass. They were then equally spaced about the circumference of the bulb. The ice-point pressure of the nitrogen thermometer at this time was somewhat higher, 727.88 mm., being a new loading. The results were in very satisfactory agreement with the first calibration, the maximum deviation being 0.04°C. It would thus appear that a properly prepared

[34] W. P. White, J. Am. Ch. Soc., **36**, p. 2011, 1914.

and protected copper-constantan thermocouple furnishes a satisfactory and reproducible method of measuring low temperatures, at least down to −183°C. To increase its applicability there ought to be a number of reliable fixed points in the low temperature range. The second part of this paper will give determinations of the freezing points of certain organic compounds with this purpose in view.

The relation between temperature and electromotive force of the couple employed was found to be represented with a maximum error of 0.18°C. by the following formula:

$$E = 0.1486(t)^{2.137} - 222.20\,t \qquad (15)$$

With the exception of the range from −37° to −91° the deviation of the values calculated from this formula from those actually observed is nowhere greater than 0.05°C. The relation can thus be used to calculate temperatures from observed electromotive forces when supplemented by a deviation plot. The data on the calibration of the thermocouple are set forth in Table XIV. The last column shows the deviations of the actually observed tem-

TABLE XIV
Thermocouple Calibration

$e_c = 0.1486t^{2.137} - 222.20t$

Date	Pressure		t_{N_2} °C	E. M. F. Observed 10^{-6} volts	E. M. F. Calculated 10^{-6} volts	$E_{cal.} - E_{obs.}$ 10^{-6} volts	$t_{cal.} - t_{obs.}$ °C
	P_o mm.	P_t mm.					
4/29/21	653.83	609.85	− 18.33	3998	3999	+ 1	+0.005
5/ 2/21	653.83	583.66	− 29.26	6303	6300	− 3	−0.014
5/ 2/21	653.83	562.23	− 38.19	8121	8129	+ 8	+0.041
4/29/21	653.83	539.54	− 47.65	9992	10015	+23	+0.117
4/29/21	653.83	507.59	− 60.97	12544	12578	+34	+0.177
4/27/21	653.83	468.54	− 77.25	15530	15556	+26	+0.146
4/28/21	653.83	424.93	− 95.43	18674	18678	+ 4	+0.024
4/29/21	653.83	370.49	−118.11	22254	22258	+ 4	+0.027
4/28/21	653.83	345.37	−125.58	23785	23791	+ 6	+0.041
4/28/21	653.83	325.62	−136.82	24941	24944	+ 3	+0.022
5/ 2/21	653.83	213.88	−183.39	30542	30543	+ 1	+0.010
7/ 8/21	654.04	214.52	−183.15	30518	30518	0	0
10/14/21	727.88	591.37	− 51.12	10671	10693	+22	+0.113
10/14/21	727.88	520.17	− 77.77	15627	15649	+22	+0.124
10/14/21	727.88	451.90	−103.33	19959	19965	+ 6	+0.037
10/14/21	727.88	379.17	−130.54	24072	24071	− 1	−0.007

peratures from those calculated by means of formula (15). The temperatures are those given by the nitrogen thermometer. In subsequent measurements with the thermocouple the temperatures were corrected so as to be in accord with the indications of the hydrogen thermometer.

Platinum Resistance Thermometer Comparison

The platinum resistance thermometer was compared with the nitrogen thermometer over the range −30°C. to −183°C. The resistance thermometer was of the flat Dickinson and Mueller type with silver sheath and steel stem of 0.010 inch wall thickness. Its resistance was measured on a Mueller dial bridge made by Wollf. The bridge coils were immersed in a stirred bath of kerosene, a thermostatic device keeping the temperature constant to ±0.03°C. No measurable heating effect of the thermometer current was detected and the galvanometer responded to changes in temperature of one or two thousandths of a degree. The ice-point resistance was found to be 25.5370 ohms, the fundamental interval 9.9606 ohms, and δ 1.51. This latter was determined from readings on the boiling point of naphthalene $[217.96° + 0.058(p - 760)]$.[35] The ice point did not shift by more than five or six ten-thousandths of an ohm during the period of several months the resistance thermometer was in use.

The results of three comparisons are given in Table XV. The general form of the deviation of the Callendar formula from the gas scale is similar to that found by Henning;[36] but the actual deviations at low temperatures are considerably less. Thus at −183°C. the platinum resistance thermometer gave indications about 1.2°C. lower than those of the nitrogen thermometer. For the actual error of the platinum thermometer at low temperatures reference should be made to its comparison with the hydrogen thermometer.

A comparison of the previously calibrated thermocouple with the corrected indications of the platinum resistance thermometer was obtained by measuring the freezing point of ammonia with each instrument. The freezing points so determined agreed within

[35] Bur. St. Circ., **35**, 1919.
[36] Henning, Ann. der Phys., **40**, p. 635, 1913.

TABLE XV

Comparison of Platinum Resistance Thermometer with Nitrogen Thermometer

Date	Pressure P_o mm.	Pressure P_i mm.	Resistance ohms	t_{N_2} °C	t_{pt} °C	$t_{N_2}-t_{pt}$ °C
11/21/21	728.07	648.37	22.5149	− 29.84	− 29.76	−0.08
11/21/21	728.07	483.47	16.1545	− 91.56	− 91.56	0
11/21/21	728.07	420.47	13.6843	−115.13	−115.27	+0.14
11/21/21	728.07	392.97	12.5962	−125.43	−125.68	+0.25
11/21/21	728.07	238.20	6.3740	−183.33	−184.49	+1.16
12/ 9/21	728.11	649.37	22.5466	− 29.48	− 29.45	−0.03
12/ 9/21	728.11	556.36	18.9815	− 64.29	− 64.23	−0.06
12/ 9/21	728.11	456.19	15.0845	−101.78	−101.83	+0.05
12/ 9/21	728.11	371.01	11.7230	−133.65	−133.95	+0.30
12/20/21	728.06	238.10	6.3699	−183.37	−184.53	+1.16
12/21/21	728.06	237.69	6.3522	−183.52	−184.70	+1.18

0.01°C. This agreement is especially satisfactory in that at this temperature (−77.8) the platinum thermometer reads higher than the gas thermometer, a fact not to be expected from the work of previous investigators. The freezing point of ammonia thus determined will be given in conjunction with the other fixed points.

Boiling Points of Carbon Dioxide and Oxygen (Preliminary)

The boiling points of carbon dioxide and oxygen were measured in a vapor pressure manometer (p. 301) with the platinum resistance thermometer. The boiling point of CO_2 at 720.2 mm. was found to be −79.21°C. on the scale of the nitrogen thermometer. The temperature-vapor pressure equation of Henning[37] for CO_2 gives −79.18°C. at this pressure. The boiling point of oxygen, corrected to normal pressure by the equation of Cath,[38] was found to be −183.55°C., while the temperature of free boiling oxygen at normal pressure was found by direct immersion of the resistance thermometer in the liquid to be −183.46°C. on the nitrogen scale.

[37] Henning, Ann. der Phys., **43**, p. 287, 1914.

For CO_2: $T=\dfrac{194.584}{1-0.14428 \log (p/760)}$

[38] Cath. Leiden Comm., **152d**, 1918.

For O_2: $\log p=-\dfrac{419.3}{T}+5.2365-0.00648T$

In view of the fact that the best previous determinations of the oxygen point all gave values between −182.90°C. and −183.00° C. our value appeared much too low. Thus the nitrogen thermometer agreed within 0.03°C. with the hydrogen thermometer of Henning, at least down to −80°C.; but at lower temperatures deviated in the direction of values which were too low. In order to determine whether this deviation was really due to a thermodynamic property of the gas, as is commonly supposed, the effect of varying the initial pressure of the gas was tried. The result of this experiment has already been given (p. 253), leading to the conclusion that the deviation was independent of the initial pressure between 640 mm. and 440 mm. No proof is thus afforded that the pressure of the nitrogen is not a linear function of the temperature at constant volume at −183°C. A deviation of the nitrogen scale from that of hydrogen at low temperatures is established, however, and the thermometer bulb was filled with hydrogen in order to obtain a direct comparison of the two scales over the whole range of the experiments.

E. Measurements with the Hydrogen Thermometer

The thermometer was loaded with hydrogen in the manner previously described for nitrogen. Owing to diffusion no attempt was made to determine the pressure coefficient experimentally, the value being obtained by calculation from the equation of state. This value at the initial pressure of 763.2 mm. is 0.0036624. Henning gives 0.0036617 for the same pressure, whereas the value calculated for 1100 mm. or 0.0036629, is in almost exact agreement with the value 0.0036628 obtained by Onnes. If the temperature of the bulb is never raised above that of the room, no serious difficulty will be caused by diffusion. Over a period of twenty days the ice-point pressure decreased at a rate of only 0.013 mm. per twenty-four hours.

Platinum Resistance Thermometer Comparison

A comparison of the platinum resistance thermometer with the hydrogen thermometer was now made. The cryostat previously described was available for measurements down to −145°C., at which point the pentane bath becomes viscous. Comparisons at

a lower temperature were carried out directly in liquid oxygen. Electrolytic oxygen was dried by phosphorus pentoxide P (Fig. 13), and forced at a pressure of about twenty pounds per square inch through the copper coil C immersed in liquid air. A continuous stream of oxygen was thus formed which could be collected in the Dewar tube D and transferred to the vessel containing the thermometers.

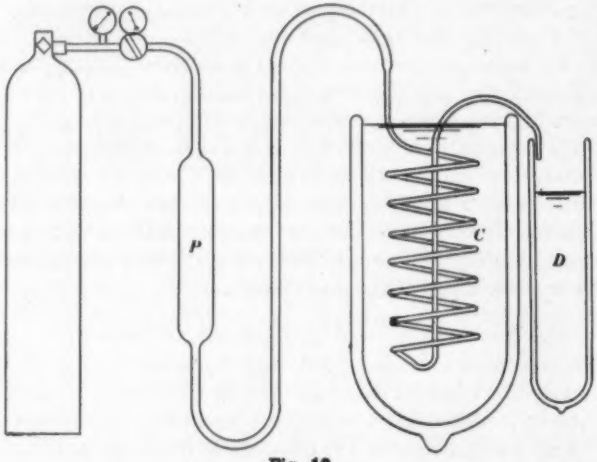

Fig. 13

The results of the comparison are given in Table XVI. Curve A of Fig. 14 exhibits the deviations of the temperatures derived from the platinum resistance thermometer and the Callendar formula from the hydrogen scale. Curve B gives the deviations of the platinum thermometer from the nitrogen scale based on Table XV and plotted against hydrogen temperatures. The deviations from the hydrogen scale are considerably larger at low temperatures than those found in the case of nitrogen, but are still smaller than the deviations found by Henning. Moreover, between 0°C. and −83°C. the resistance thermometer reads too high, whereas Henning found no deviation between 0° and −40° and below the latter temperature the resistance thermometer indicated increasingly too low temperatures.

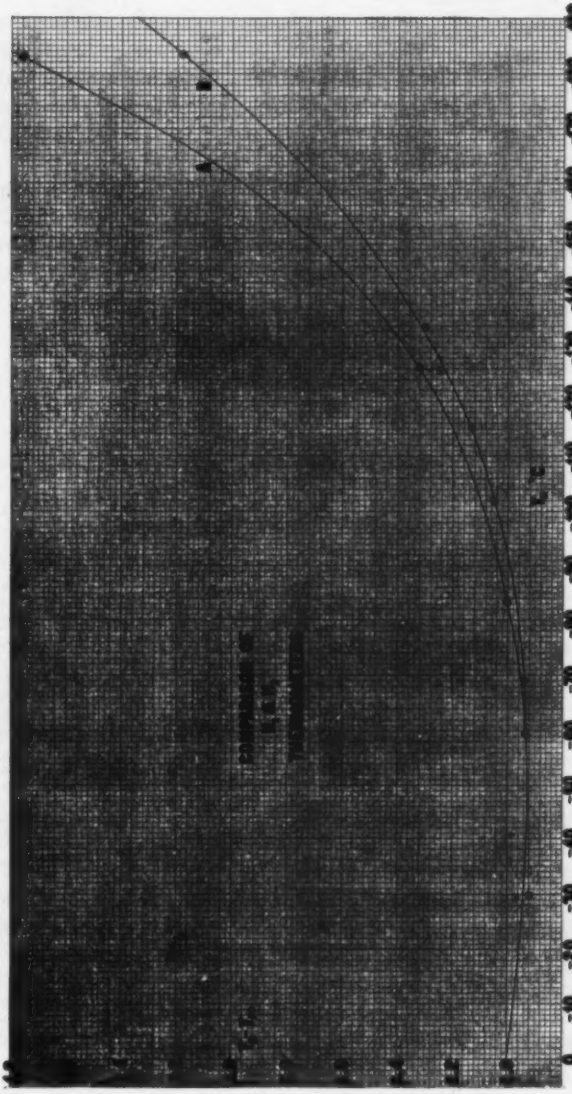

Fig. 14

The deviations of a platinum resistance thermometer must be, to a certain extent, dependent upon the particular instrument employed, since they are certainly in part caused by strains in the wire, due to unequal contraction on its support. Thus the results of Henning and the above measurements clearly indicate a large deviation of the platinum resistance thermometer at low temperatures of the approximate magnitude given, and, furthermore, that the deviations of any particular instrument must be independently investigated. A type of support which would not set up strains in the wire under large temperature changes would be a great advantage, and the deviations of an instrument so constructed might possibly possess a considerable degree of generality.

TABLE XVI
Comparison of Platinum Resistance Thermometer with Hydrogen Thermometer

Date	*Pressure* P_o *mm.*	*Pressure* P_t *mm.*	*Resistance ohms*	t_{H_2} °C	t_{pt} °C	$t_{H_2}-t_{pt}$ °C
4/ 6/22	763.20	596.93	19.4758	− 59.48	− 59.41	−0.07
4/ 6/22	763.20	530.89	17.0288	− 83.11	− 83.11	0
4/ 6/22	763.20	410.67	12.5120	−126.12	−126.44	+0.32
3/20/22	763.23	251.67	6.348	−183.01	−184.85	+1.84
3/20/22	763.23	251.77	6.352	−182.97	−184.81	+1.84
3/20/22	763.23	251.80	6.354	−182.96	−184.79	+1.83
3/30/22	763.17	252.82	6.386	−182.60	−184.36	+1.76
3/30/22	763.16	252.57	6.377	−182.68	−184.45	+1.77

Comparison of Nitrogen and Hydrogen Thermometers

The platinum resistance thermometer having been carefully compared with the nitrogen and hydrogen thermometers under exactly similar conditions, we are now in a position to find the deviations of the nitrogen scale from that of hydrogen. These can be found directly from Fig. 14 and are, for convenience, tabulated in Table XVII. As had been expected from the previous measurements with the nitrogen thermometer, there is no difference in the indications of the two instruments down to −70°C. At −80° the difference amounts to 0.02° and increases more and

more rapidly with lowering temperatures until at the oxygen point it becomes 0.60°. Furnished with these deviations we can now correct all temperatures measured with the thermocouple to the scale of the hydrogen thermometer.

The deviations of the nitrogen thermometer from the hydrogen scale will be ascribed, by those familiar with gas thermometry, to a property of the gas itself; although there is difficulty in explaining the difference of 0.60° at −183° in view of the fact that the Berthelot correction at this temperature and initial pressure would be somewhat less than 0.4°. The usual interpretation is rejected, however, in view of the facts presented. Within the limits of

TABLE XVII
Deviations of the Nitrogen Thermometer from the Hydrogen Scale

t_{H_2} °C	$t_{H_2}-t_{N_2}$ °C	t_{H_2} °C	$t_{H_2}-t_{N_2}$ °C
− 70	+0.01	−140	+0.14
− 80	+0.02	−150	+0.19
− 90	+0.04	−160	+0.28
−100	+0.05	−170	+0.40
−110	+0.06	−180	+0.55
−120	+0.08	−183	+0.60
−130	+0.10		

experimental measurements it has been found that the isometrics of gases sufficiently removed from their condensation points are straight lines. Direct experimental evidence, moreover, of a thermodynamic correction could not be found, in that the indications of the nitrogen thermometer at −183°C. were independent of a large change in the initial pressure. Other possible causes of the divergence in the two gas thermometers are evident since condensible impurities in the gas, association, and adsorption would all cause a similar effect. Inasmuch as the gas was carefully prepared and passed through liquid air before being admitted to the bulb, the possibility of condensible impurities in sufficient amount to seriously affect the results must be ruled out. At −183° and a pressure of a third of an atmosphere the gas is still far enough from its condensation point to make it improbable that association of the molecules could more than partly account

for the deviations. That adsorption takes place at low temperatures is well known, and it is of interest to form an estimate of how much adsorption would be necessary to explain the observed deviation. The area of the bulb is approximately 120 sq. cm. and taking the area occupied by one molecule to be $(3\times10^{-8})^2$ it is found that there would be 13.3×10^{16} molecules in one adsorbed layer. This corresponds to 6.14×10^{-6} grams per layer. If the pressure is decreased by Δp due to adsorption, the total fraction of gas adsorbed is $\Delta p/p$. The total number of grams adsorbed to produce a lowering of the pressure by Δp will then be $\frac{\Delta p}{RT}.\ v$ or $31.5\frac{\Delta p}{T}$. Hence the number of layers necessary to account for the effect is $\frac{31.5}{6.14\times10^{-6}}\cdot\frac{\Delta p}{T}=5.13\times10^{6}\frac{\Delta p}{T}$, where Δp is expressed in atmospheres.

TABLE XVIII
Adsorption of Nitrogen

$$L=5.13\times10^{6}\frac{\Delta p}{T}$$

T_H Degrees Kelvin	T_H-T_N	ΔP mm.	Number of Layers
203	.01	.03	1
193	.02	.05	2
183	.04	.11	4
173	.05	.13	5
163	.06	.16	7
153	.08	.21	9
143	.10	.27	13
133	.14	.37	19
123	.19	.51	28
113	.28	.75	45
103	.40	1.07	70
93	.55	1.47	106
90	.61	1.63	122

In Table XVIII are given the number of layers of nitrogen adsorbed necessary to account for the deviation of the nitrogen from the hydrogen thermometer on the assumption that adsorption is negligible in the latter case. These must be regarded as

maximum values since the area of the bulb surface calculated from its dimensions is a lower limit. The effective area for adsorption may be several times as great owing to the unevenness of the surface with respect to molecular dimensions. Thus it would not be unreasonable to suppose that due to this circumstance the deviation at −183°C. might be accounted for by adsorption to a depth of only thirty or forty layers. Whether adsorption of nitrogen and other gases on quartz at low temperatures takes place to such an extent is of course an open question. No reliable data are at hand. Langmuir,[39] however, found that glass and mica strongly adsorbed nitrogen at liquid air temperatures at only 0.1 mm. pressure; while the adsorption of hydrogen he found to be very much less. It thus appears that the deviation of the nitrogen

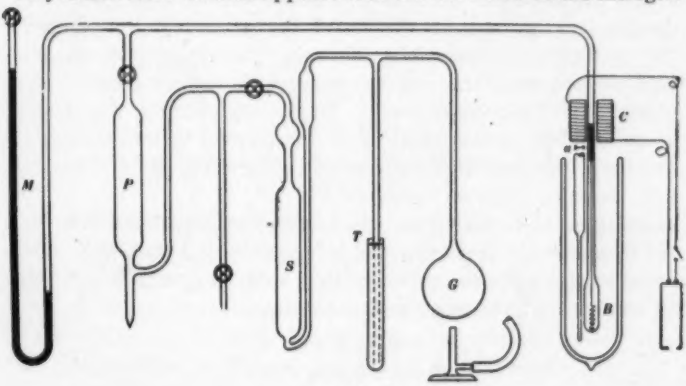

Fig. 15

thermometer from the hydrogen scale at low temperatures finds a ready explanation in the combined effects of adsorption and association.* Of these two the former would appear to be the larger. In the case of the hydrogen thermometer the indications are that any error due to adsorption at liquid air temperatures is extremely small.

[39] Langmuir, J. Am. Ch. Soc. **39**, 1917.

*That variation of the inital pressure is without effect is due to adsorption being independent of the pressure above a certain point. Thus, on metals the amount of gas adsorbed remains constant above a pressure of 300 mm. according to Taylor and Burns, J. Am. Ch. Soc., **43**, p. 1273, 1921.

The Boiling Point of Oxygen

A determination of the boiling point of oxygen based on the nitrogen thermometer has already been noted. It is now possible to transfer this to the hydrogen (thermodynamic) scale. The determination was carried out by means of the apparatus shown in Fig. 15. The oxygen was prepared in G by the decomposition of potassium permanganate. It was passed through sodium hydroxide (20 per cent) S, and phosphorus pentoxide P and condensed in the bulb B (ca. 10 c.c.) surrounded by liquid air. The tube T, dipping into mercury, acted as a valve, limiting the pressure to about ninety centimeters of mercury. The liquid in B could be electromagnetically stirred by means of the iron stirrer a and the coils C. The vapor pressure of the liquid was read directly on the manometer M and its temperature found with the platinum resistance thermometer. The apparatus was exhausted and swept out several times with oxygen before proceeding with the measurements. To test the purity of the oxygen about one-half of the liquid in B was allowed to evaporate and the vapor pressure of the remainder determined, being found to give the same value as before.

The normal boiling point of oxygen thus found is 182.94°C., the details of the measurements being given in Table XIX. The agreement of our value with the latest value of Onnes,[40] −182.93° C. (or −182.97° uncorrected), is excellent.

TABLE XIX
Oxygen Boiling Point

Date	$t_{pt.}$ °C	t_{H_2} °C	*Vapor Pressure mm.*	$\frac{\Delta p_i}{\Delta t}$ *mm./deg.*	*N.B.P.* °C
12/23/21	−184.41	−182.64	784.4	81.8	−182.94
12/23/21	−184.36	−182.60	787.9	82.3	−182.94

The Boiling Point of Carbon Dioxide

The boiling point of carbon dioxide was determined in the same vapor pressure manometer that was used for oxygen. The gas

[40] Cath., Leiden Comm., **152d**, see Note 1, p. 48.

was prepared by the decomposition of sodium bicarbonate and dried with phosphorus pentoxide. The bulb (Fig. 15) was immersed in a freezing mixture of carbon dioxide snow and ether, whereupon the carbon dioxide condensed in the form of perfectly clear ice. The vapor pressure was found independent of the amount of substance, thus attesting to its purity. Observations were taken at a pressure of 720.2 mm. and the boiling point at this pressure was found to be −79.19°C. on the hydrogen scale. This is in excellent agreement with the value of −79.18°C. given by the formula of Henning.[37] The details of the measurements follow:

Boiling Point of Carbon Dioxide

Date	t_{pt}	t_{H_2}	*Vapor Pressure mm.*	$\frac{\Delta p}{\Delta t}$ *mm./deg.*	*N.B.P. °C*
1/12/22	−79.17	−79.17	720.2	60.3	−78.53

Part II

Freezing Points of Certain Organic Liquids and of Mercury and Ammonia

Certain freezing points have been measured in the range from 0°C. to −123°C. in order to establish fixed points for thermometric comparison. The temperatures were obtained with the multiple copper-constantan thermocouple described in Part I, p. 290, which had been repeatedly calibrated directly against the nitrogen constant volume thermometer. A direct comparison of the nitrogen and hydrogen thermometers enables us to give the freezing points directly on the constant volume hydrogen, or thermodynamic, scale.

The Method

The electrical circuit has been described as noted above. The liquid whose freezing point is to be determined is contained in the double-walled vessel *A* (Fig. 16A), 2 cm. in diameter and 13 cm. long. The space between the walls of this vessel is connected to the vacuum pump and can be exhausted to any desired degree, thus controlling the rate of cooling. Cooling is obtained by liquid

air in the outer Dewar tube *B*. The liquid is stirred by a stream of dry air entering through the fine glass tube *S*, further serving to keep the space above the liquid free of moisture. It was found that the freezing points were independent of the rate of stirring between wide limits, but that some stirring was necessary to give concordant results. In determining the freezing points of organic liquids a thermocouple possesses a marked advantage in that it records the temperature at a definite point. The thermal conductivity of the two phase mixtures is so low that it is practically impossible to secure uniformity of temperature throughout a large mass of the liquid as the freezing point is approached and an instrument of considerable bulk will consequently register an average temperature which may not be the true freezing point, at least in those cases where ice forms first at the bottom of the tube and builds upward.

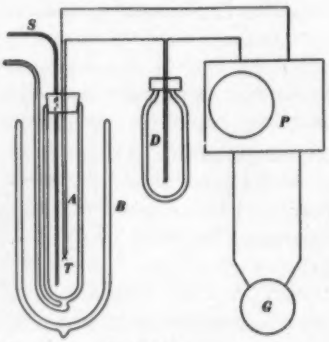

Fig. 16a

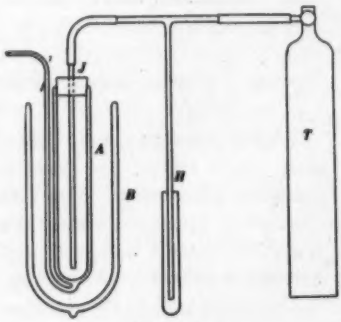

Fig. 16b

In determining the freezing points of liquids which are gaseous at ordinary temperatures, such as methyl chloride and ammonia, the tube *A* was first well cooled, whereupon the gas from the supply *T* (Fig. 16B) was admitted through the glass tube *J*. It then rapidly liquefied under the slight excess of pressure. The tube *H*, dipping into mercury, prevented the pressure from becoming more than a few centimeters of mercury above atmospheric.

The Results

The individual determinations are given in Tables XX-XXX. The methods of purification, starting with the best C. P. chemicals obtainable, are also given.* Column 5 gives the average cooling rate during the five minutes preceding freezing. The freezing points of mercury, ammonia, and methyl chloride are easily reproducible and constitute the most satisfactory fixed points. The ammonia point was likewise measured with the platinum resistance thermometer, the two methods agreeing within 0.01°C. In some measurements a silvered tube was used in place of the clear glass Dewar tube *A* without affecting the results. A considerable variation in the dimensions of the freezing point tube was likewise without effect on the constancy of the freezing points. The freezing point found for an organic liquid depends somewhat upon the method employed and the thoroughness of the purification. The results here given will be found reproducible provided the general method of procedure is followed.

In Table XXXI the various fixed points are summarized, including the determinations of the boiling points of carbon dioxide and oxygen recorded in Part I. For the sake of comparison the results of other investigators are also given.

TABLE XX

Carbon Tetrachloride†
CCl_4

Date	*E.M.F.* 10^{-6} *Volts*	*Time Minutes*	*Cooling Rate Deg./Min.*	*Freezing Point °C*
5/25/21	4957	8	0.67	−22.85
5/25/21	4962	9	0.73	−22.86
6/ 6/21	4960	7	0.77	−22.86
6/ 6/21	4959	7	1.03	−22.86
6/ 6/21	4965	5	2.14	−22.89
6/ 6/21	4966	5	2.44	−22.89

* The chemicals were kindly prepared by Mr. R. S. Taylor of the Research Laboratory of Physical Chemistry.

† *Purification.* Warm with alcohol and caustic potash to remove CS_2 and SCl_2. Remove alcohol by shaking with water. Remove water over caustic potash and finally over sodium, lastly distill over paraffin, whereby the small quantity of perchlorethane is held back.

TABLE XXI

Mercury*

Hg.

Date	*E.M.F.* 10^{-6} *Volts*	*Time Minutes*	*Cooling Rate Deg./Min.*	*Freezing Point °C*
6/24/21	8264	Indefinite	1.29	−38.90
6/24/21	8264	Indefinite	1.57	−38.90
8/30/21†	8262	Indefinite	1.51	−38.89
8/30/21†	8264	Indefinite	0.98	−38.90

* *Purification.* Agitate with dilute nitric acid and distill several times.
† Silvered tube.

TABLE XXII

Chlorbenzene*

C_6H_5Cl

Date	*E.M.F.* $\times 10^{-6}$ *Volts*	*Time Minutes*	*Cooling Rate Deg./Min.*	*Freezing Point °C*
5/16/21	9590	31	2.40	−45.58
5/17/21	9584	30	1.79	−45.53
6/ 7/21	9595	10	3.17	−45.62
6/ 7/21†	9590	12	3.65	−45.58
6/ 7/21	9590	50	2.89	−45.58
6/ 9/21†	9590	10	1.04	−45.58
8/26/21†	9589	5	2.54	−45.57

* *Purification.* Wash with water and dilute *NaOH*. Dry over $CaCl_2$ and distill with fractionating column three or four times. Dry over metallic sodium and again distill.
† Silvered tube.

TABLE XXIII

Chloroform*

$CHCl_3$

Date	*E.M.F.* 10^{-6} *Volts*	*Time Minutes*	*Cooling Rate Deg./Min.*	*Freezing Point °C*
5/20/21	13141	2	1.34	−64.15
5/20/21	13160	8	0.05	−64.24
5/20/21	13147	12	2.11	−64.17
5/20/21	13134	3	0.82	−64.11
6/ 8/21	13151	2	1.67	−64.20
6/ 8/21	13160	2	2.13	−64.24
6/ 8/21	13149	3	1.03	−64.18
6/ 9/21	13157	4	1.04	−64.23
6/ 9/21	13154	8	1.48	−64.21
6/ 9/21	13154	3	1.56	−64.21

* *Purification.* Agitate with pure concentrated H_2SO_4 until the acid is no longer colored. Next wash with Na_2CO_3 and then with alkaline permanganate. Wash with distilled water, dry over sodium and distill.

TABLE XXIV

Ammonia*

NH_3

Date	E.M.F. 10^{-6} Volts	Time Minutes	Cooling Rate Deg./Min.	Freezing Point °C
6/20/21	15634	28	0.81	−77.80
6/20/21	15634	25	0.80	−77.80
8/25/21 †	15635	6	1.28	−77.80
8/25/21 †	15634	33	1.05	−77.80

* *Purification.* Dry with sodium.
† Silvered tube.

TABLE XXV

Toluene*

$C_6H_5CH_3$

Date	E.M.F. 10^{-6} Volts	Time Minutes	Cooling Rate Deg./Min.	Freezing Point °C
5/13/21	18729	5	0.76	−95.71
5/16/21	18730	5	1.28	−95.71
5/31/21	18730	4	0.79	−95.71
6/ 4/21	18723	4	2.33	−95.67
6/ 9/21 †	18726	4	1.58	−95.68
6/22/21	18734	13	0.71	−95.73
6/22/21	18730	10	1.21	−95.71
7/19/21	18728	6	1.58	−95.70
7/19/21	18726	11	1.27	−95.69
8/31/21 †	18727	12	0.57	−95.69

* *Purification.* Free of phenols by *NaOH*. Shake with concentrated H_2SO_4 until acid is no longer colored. Agitate with mercury until it ceases to pollute a clean *Hg* surface. Wash and distill several times. Dry with $CaCl_2$ and sodium.
† Silvered tube.

TABLE XXVI

Methyl Chloride*

CH_3Cl

Date	E.M.F. 10^{-6} Volts	Time Minutes	Cooling Rate Deg./Min.	Freezing Point °C
6/23/21	19172	5	1.28	−98.39
6/23/21	19172	11	0.84	−98.39

* Taken from the top of a tank of the commercially pure gas.

TABLE XXVII

Methyl Alcohol*

CH_3OH

Date	E.M.F. 10^{-6} Volts	Time Minutes	Cooling Rate Deg./Min.	Freezing Point °C
6/17/21	19197	6	1.01	−98.54
6/17/21	19194	8	1.03	−98.53

* *Purification.* Treat with iodine and then with slight excess *NaOH*. Reflux over fresh quicklime and finally dry with metallic calcium. Keep moist air away.

TABLE XXVIII

Carbon Disulphide*

CS_2

Date	E.M.F. 10^{-6} Volts	Time Minutes	Cooling Rate Deg./Min.	Freezing Point °C
6/16/21	21484	2	2.54	−112.96
6/16/21	21486	3	2.49	−112.97
6/16/21	21483	4	0.62	−112.95
6/17/21	21488	3	0.40	−112.97
8/27/21†	21491	8	1.10	−113.00
8/27/21†	21488	5	0.68	−112.98

* *Purification.* Digest with finely divided copper powder or with mercury over a water bath. Distill repeatedly. Dry with $CaCl_2$ and *Na*.

† Silvered tube.

TABLE XXIX

Ether*

$(C_2H_5)_2O$

Date	First Modification†		Cooling Rate Deg./Min.	Freezing Point °C
	E.M.F. $\times 10^{-6}$ Volts	Time Minutes		
6/13/21	23052	7	1.47	−123.40
6/15/21	23052	27	1.58	−123.40
6/15/21	23046	5	1.60	−123.36
6/15/21	23054	28	1.76	−123.42
6/16/21	23053	15	1.33	−123.41

* *Purification.* Shake with conc. H_2SO_4. Then leave with 200 c.c. of a sat. sol. of $KMnO_4$ containing 20 gms. of *NaOH* per liter. After 24 hours decant and repeat. Wash with water. Let stand over H_2SO_4 shortly. Dry over $CaCl_2$, then distill and dry over sodium.

† The first modification occurred more often and gave the better point although the second modification is considered the more stable (see Table XXX).

Date	Second Modification		Cooling Rate Deg./Min.	Freezing Point °C
	E.M.F. $\times 10^{-6}$ Volts	Time Minutes		
6/13/21	21890	20	—	−115.6
6/13/21	21921	39	0.37	−115.7
6/15/21	21990	17	1.60	−116.3

TABLE XXX

Detail of Ether Run Showing Both Modifications

6/15/21

Time in Minutes	Reading in Microvolts	Time in Minutes	Reading in Microvolts	Time in Minutes	Reading in Microvolts	Time in Minutes	Reading in Microvolts
0	22395	8	23036 *	16	21988†	24	21991†
1	22650	9	23050 *	17	21991†	25	21993†
2	22859	10	21996	18	21990†	26	21994†
3	23069	11	21987 †	19	21990†	27	21992†
4	23243 *	12	21987 †	20	21990†	28	21991†
5	23054 *	13	21990 †	21	21990†	29	22010
6	23039 *	14	21991 †	22	21991†	30	22064
7	23049 *	15	21991 †	23	21991†	31	22164

* One. † Two.

TABLE XXXI

Fixed Points Between O°C and −183°C Absolute Centigrade Temperatures

Substances	*K, T, & Y*	*Henning*[37]	*Onnes*[39]	*Timmerman's*[40]	*Brill*[41]	*Wilhelm*[42]	*Travers,*[29] *Senter and Jacquerod*
Carbon Tetrachloride, CCl_4	− 22.87			− 22.90			
Mercury	− 38.90	− 38.89				−38.87	
Chlorbenzene, C_6H_5Cl	− 45.58	− 45.54		− 45.2			
Chloroform, $CHCl_3$	− 64.19	− 63.7		− 63.5			
Ammonia, NH_3	− 77.80				77.7		
Carbon Dioxide, CO_2(N.B.P.)	− 78.53	− 78.52					
Toluene, $C_6H_5CH_3$	− 95.70			− 95.1			
Methyl Chloride, CH_3Cl	− 98.39						
Methyl Alcohol, CH_3OH	− 98.54*			− 97.1			
Carbon Disulphide, CS_2	−112.97†	−112.0		−111.6			
Ether (First Mod.) $(C_2H_5)_2O$	−123.40	−123.65					
Ether (Second Mod.)	−115.9			−116.3			
Oxygen (N.B.P.)	−182.94	−182.97	−182.93				−182.93

[37] Ann. d. Phys., **43**, p. 282, 1914.
[39] Leiden Comm., **107a**, gives −182.99. (This has been corrected to −182.93 in L. C. 152d, p. 48, 1918.)
[40] C. r., **174**, p. 365, 1922.
[41] Ann. d. Phys., **21**, p. 170, 1906.
[42] Bull. Bur. St., **13**, p. 665, 1917.
[29] Phil. Trans. A, **200**, p. 105, 1903.
* Too hygroscopic for ready reproducibility.
† Reproducibility uncertain, owing perhaps, to small heat of fusion and difficulties of purification.

Summary

A discussion of the constant volume gas thermometer and its errors has been given. Evidence has been cited leading to the conclusion that the pressure of a gas at constant volume is a linear function of the temperature, in which case the constant volume gas thermometer indicates directly on the thermodynamic scale. This conclusion has been supported by: first, an analysis of the isometrics of hydrogen calculated from the data of the Leiden laboratory; second, a recalculation of the boiling point of sulphur based on the data of the H_2, He and N_2 constant volume and the N_2 constant pressure gas thermometers (mean N. B. P. 444.56°), in which the value obtained from the constant volume nitrogen thermometer of Holborn and Henning, recalculated using the expansion coefficient given by the equation of state for nitrogen, was found to agree almost exactly, without correction to the thermodynamic scale, with the constant pressure nitrogen value of Eumorfopoulos corrected to the thermodynamic scale in accordance with the Keyes equation of state for nitrogen and with the value of Holborn and Henning derived from the constant volume helium and hydrogen thermometers; third, by direct experiment in which the indications of a constant volume nitrogen thermometer at −183° were found independent of the initial pressure between 640 and 440 mm.

A constant volume hydrogen thermometer, capable of measuring temperatures with an accuracy of 0.01 per cent, has been described, together with a new form of cryostat in which low temperatures can be held constant to within 0.01°.

The copper-constantan thermocouple has been calibrated against the gas thermometer and the deviations of the platinum resistance thermometer from the absolute scale determined over the range from 0° to −183°. The platinum thermometer has been found to give too low a temperature at the boiling point of oxygen by about 1.6°; but the exact deviation depends upon the particular instrument employed.

A direct comparison of the nitrogen and hydrogen constant volume thermometers showed no divergence between the two scales down to −70°, while below this temperature the divergence

gradually increases until it amounts to 0.6° at the boiling point of oxygen. It has been shown that this divergence can be readily explained by the combined effects of association of the nitrogen and adsorption upon the walls of the quartz container.

The normal boiling point of carbon dioxide has been found to be −78.53°C. and that of oxygen −182.94°C. A detailed account has been given of a method of determining freezing points of various substances in the interval from −40° to −124° to serve as fixed points for thermometric comparison. These freezing points are:

Carbon Tetrachloride, CCl_4	− 22.87
Mercury	− 38.90
Chlorbenzene, C_6H_5Cl	− 45.58
Chloroform, $CHCl_3$	− 64.19
Ammonia, NH_3	− 77.80
Toluene, $C_6H_5CH_3$	− 95.70
Methyl Chloride, CH_3Cl	− 98.39
Methyl Alcohol, CH_3OH	− 98.54
Carbon Disulphide, CS_2	−112.97
Ether $(C_2H_5)_2O$, I. Mod	−123.40
Ether, II. Mod	−115.9

Helium has been found to diffuse too readily through quartz at room temperatures to permit of its convenient use in a thermometer bulb of this material. Hydrogen likewise has been found to diffuse through quartz at ordinary temperatures, but so slowly as not to interfere with its use in quartz for low-temperature thermometry.